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CHAPTER I

INTRODUCTION

The adsorption of hydrocarbon gases on solid adsorbents has been used by the petroleum industry in recent years to effect field as well as laboratory separations of the heavier hydrocarbon components from a natural gas stream. Such process gas streams generally are predominately light components, often containing 85-90 per cent or more of methane. The design of suitable adsorption columns requires a knowledge of the equilibrium adsorbent capacity for the components and systems of interest, under conditions approximating those expected in actual field applications. In the past, the design and evaluation of such adsorption units has been hampered by the lack of suitable and applicable equilibrium data, and the prediction techniques used have been based, more or less, upon engineering judgment, a few pertinent dynamic data, and workable rules-of-thumb. In such engineering work, it has become increasingly apparent that studies of adsorption, particularly for hydrocarbon gas mixtures in static systems, would provide much needed data and information. For this, theoretical models of adsorption may be substantiated or further developed, and more reliable prediction techniques may be evolved.

The primary objective of the present study was to provide such equilibrium data and to determine the most useful model for predicting adsorption isotherms. Another objective was to compare such data with existing dynamic data to determine whether any correlation exists between the two systems. If so, then it seems reasonable to expect the static data to provide a satisfactory means of predicting maximum adsorptive capacity under dynamic conditions.

The literature search revealed numerous articles related to the adsorption process under a rather wide variety of conditions. However, practically all of the past work has been in systems of single component gases. Few data have been presented for systems of hydrocarbon gas mixtures which would permit the reliable prediction of adsorption for such systems. It is in this latter realm of adsorption, though, that equilibrium data are necessary if any reliable theoretical, or empirical, basis for future prediction techniques is drawn. Actually, only one really pertinent article, dealing with multicomponent adsorption in systems of interest, was found in the literature. This information, published only recently, provided a partial theoretical basis for the present work and will be discussed in a later chapter.

In order to minimize the amount of data needed for satisfactory evaluations of the theory involved, it was necessary to minimize the number of variables involved in the investigation. In doing so, it was decided to limit the investigation to only one equilibrium temperature, 100°F, and only one solid adsorbent, Davison 03 Grade Silica Gel, which is widely used in commercial adsorption units in the petroleum industry. Pressures to 1014 psia were used to investigate the adsorption behavior of binary mixtures of methane and n-butane,

n-pentane, and n-hexane. Ternary mixtures of methane, n-pentane, and n-hexane were also used to provide a basis of checking the validity of the prediction technique so presented.

The experimental data and results were analyzed and correlated with the purpose of determining a suitable adsorption prediction technique which has practical engineering value and, at the same time, clarifies the factors governing equilibrium adsorption behavior. It is believed that such objectives have been accomplished, and the technique presented will be of great value to engineers in the future design of hydrocarbon adsorption units.

It should be pointed out that the data and results presented herein are applicable, strictly, to 03 type silica gels. The extension of these data to other adsorbents is questionable and can be fully substantiated only by further experimental studies of this nature.

CHAPTER II

THEORY

Physical adsorption of gases or vapors on solids is a phenomenon whereby molecules from the gas or vapor phase attach themselves to the surfaces of the solid as the result of forces of attraction between the solid and adsorbate molecules. Such adsorption processes involve little or no chemical interaction between the adsorbate and adsorbent of the type present with chemisorption. Physical adsorption may be considered as the accumulation of a given component at the interface of two phases, whether it be a gas-solid, gas-liquid, liquid-solid, or liquid-liquid interface. In the present study, only the adsorption phenomenon at gas-solid interfaces is considered. Such processes have been considered in great detail in the reported literature, although little information is available for the systems studied.

Numerous attempts have been made to describe the underlying physical model of adsorption by both theoretical and/or experimental studies of single component adsorbates. The physical models of adsorption have been discussed in numerous books, the most comprehensive of which are those of Brunauer (3), Adamson (1), and Young and Crowell (13).

The amount of gas or vapor adsorbed at equilibrium, at any given pressure and temperature, depends upon the nature of the adsorbent and

adsorbate and the type of surface forces acting at the gas-solid interface. In the absence of "retrograde" effects the amount absorbed generally increases with pressure and decreases with increasing temperature, due to the exothermic nature of all adsorption processes. The amount of gas adsorbed on the surface of a non-porous solid is basically determined by the number of collisions of adsorbate molecules with the solid surface and the average time of stay of the molecules on the surface, which has been given by Frenkel and discussed by de Boer (2) and Adamson (1) as

$$\tau = \tau_o \exp(Q/RT) \qquad (1)$$

where τ_o represents the time of stay on the surface when no attractive forces exist between the solid and adsorbate molecules. The time τ_o has been estimated to be of the order of molecular vibration times of about 10^{-13} seconds. The quantity Q represents the heat of adsorption, i.e., the interaction energy at the gas-solid interface. Both τ_o and Q are functions of the particular adsorbent surface under consideration.

Brunauer (3) has pointed out that all adsorption processes are exothermic due to the spontaneous nature of the adsorption process and resulting decrease in the free energy of the system. In physical adsorption processes the heat of adsorption is about one-third greater than the heat of condensation of the gas, and the forces involved between adsorbent and adsorbate are analogous to those in condensation phenomena. Actually, the adsorbed phase may be considered as a pseudo-liquid, or liquid-like, phase experiencing a type of vapor-liquid equilibrium, but probably does not approximate that existing between a

vapor and its equilibrium liquid phase. Generally, however, the vapor-adsorbate equilibrium will not be the same as the vapor-liquid equilibrium due to the action of the interfacial forces involved. Comprehensive discussions of the forces involved in adsorption processes have been presented by numerous authors, more recently by Payne (31) and Adamson (1).

Several empirical and theoretical techniques are available in the literature, all of which attempt to provide a basis for understanding the nature of the interaction of the adsorbent and adsorbate. The oldest isotherm equation, still very much in use in many applications today, is Freundlich's equation (6). This equation is strictly empirical, although numerous attempts have been made to develop a theoretical basis for it. This equation is:

$$v = k'P^{1/n} \tag{2}$$

If the Freundlich equation is re-written in the form

$$\log v = \log k' + (1/n)\log P \quad , \tag{3}$$

it is evident that a plot of log v versus log P will produce a straight line if the experimental data fit the Freundlich equation.

Perhaps the first satisfactory theoretical model of adsorption was presented by Langmuir (12) in 1915. He believed that the cause of adsorption was due to the interaction of unsatisfied fields of force on the solid surfaces with the gaseous molecules striking the surface. In cases where the surface forces are intermolecular in nature, physical adsorption is involved, and where the forces are interatomic in nature,

chemical adsorption is generally predominant. Langmuir further pointed out that these forces are very short range in character (a few angstrom units), so that once the field of force is satisfied by the adsorption of gas molecules on the surface, no significant forces exist for the attraction of further molecular layers. This argument formed the basis of Langmuir's monolayer adsorption theory, which may be expressed as:

$$v = v_m bP/(1 + bP) \tag{4}$$

where v_m represents the amount adsorbed when a complete monolayer has been formed, and P is the system equilibrium pressure. The constant b is given by

$$b = N\sigma^{\circ}\tau_o \, (1/2\pi RTM)^{1/2} \exp(Q/RT). \tag{5}$$

For handling experimental data, the Langmuir equation may be expressed in the form

$$P/v = 1/bv_m + P/v_m \tag{6}$$

such that a plot of P/v versus P gives a straight line for a proper fit, from which the constants, b and v_m, may be evaluated.

The Langmuir equation is applicable for pure component gases, and Adamson (1) has suggested an equation whereby the theory may be extended to a mixture of gases (provided the individual b and v_m constants can be evaluated from single component data) as follows:

$$v_i = v_{mi} b_i P_i \; / \; (1 + \Sigma b_i P_i) \quad . \tag{7}$$

For testing the experimental data of binary gas mixtures, the Langmuir isotherm may be obtained as follows:

Let θ_1 and θ_2 be the fractions of adsorbent surface covered by adsorbates 1 and 2, respectively. Then, the bare surface will be $1 - \theta_1 - \theta_2$.

Rate of adsorption of gas 1 = $k_1 P_1 (1 - \theta_1 - \theta_2)$.

Rate of adsorption of gas 2 = $k_2 P_2 (1 - \theta_1 - \theta_2)$.

P_1 and P_2 are partial pressures of gases 1 and 2, respectively.

Rate of desorption of gas 1 = $k'_1 \theta_1$.

Rate of desorption of gas 2 = $k'_2 \theta_2$.

Then, at equilibrium,

$$k_1 P_1 (1 - \theta_1 - \theta_2) = k'_1 \theta_1 \quad , \text{ and}$$

$$k_2 P_2 (1 - \theta_1 - \theta_2) = k'_2 \theta_2 .$$

Then, $$\theta_1 = b_1 P_1 / (1 + b_1 P_1 + b_2 P_2) \tag{8}$$

and $$\theta_2 = b_2 P_2 / (1 + b_1 P_1 + b_2 P_2), \tag{9}$$

which upon dividing becomes,

$$\theta_1 / \theta_2 = K' \, P_1 / P_2 . \tag{10}$$

If the experimental data fit the monolayer adsorption theory of Langmuir, then a plot of θ_1/θ_2 versus P_1/P_2, as given by Equation 10, plots as a straight line through the origin. This affords a rapid means of correlating experimental data, or at least to determine whether the monolayer is obeyed. The constant K' may also be evaluated from such a

plot.

Adamson (1), as well as other authors, has summarized the principal postulates of the Langmuir isotherm as follows:

(1) "The energy of adsorption is constant (which implies uniform sites and no interactions between adsorbate molecules)."

(2) "The adsorption is on localized sites (which implies no translational motion of adsorbate molecules in the plane of the surface)."

(3) "The maximum adsorption possible corresponds to a complete monomolecular layer."

Brunauer (15), who developed the BET theory of multimolecular adsorption, to be discussed later, has pointed out that practically all writers of books and papers on adsorption processes have repeated the first two postulates above, and presume that the Langmuir and BET theories assume uniform surface and no interactions between molecules. On the contrary, Brunauer has stressed that neither the BET nor the Langmuir theory makes such assumptions. These assumptions have become associated with these theories as the result of derivations by statistical mechanics. Brunauer admits that the theories do, indeed, assume a constant heat of adsorption over the entire layer, but such an assumption should not lead to the conclusion of uniform surface and no molecular interaction, because constant heats of adsorption may be obtained in other ways, even with heterogeneous surfaces. These remarks of Brunauer tend to remove some of the past serious objections to these adsorption theories.

The BET [Brunauer-Emmett-Teller] (16) theory of adsorption is summarized in numerous textbooks and articles dealing with adsorption processes. This theory was devised to account for some of the apparent shortcomings of the Langmuir isotherm by assuming that adsorption may occur in multimolecular layers. One of the most important postulates of the BET theory is that each layer of adsorption behaves individually as a Langmuir isotherm. The heat of adsorption of the first layer may have some special value, Q, while the second and subsequent layers may have heats of adsorption approximating condensation or evaporation of liquid adsorbates, with condensation or evaporation occurring only on exposed surface sites. The BET isotherm may be expressed, for single components, as:

$$v/v_m = cx \;/\; (1 - x)(1 + (c - 1)\, x) \qquad (11)$$

where $x = P/P_o$, and P_o is the saturation vapor pressure of the pure liquid adsorbate. The BET equation may be put in the form:

$$x/v\,(1 - x) = 1/cv_m + (c - 1)\, x/cv_m \qquad (12)$$

such that a plot of x/v(1-x) versus x produces a straight line, if the data fit, from which the constants c and v_m may be evaluated. For the special case where monolayer adsorption exists, the BET equation very appropriately reduces to the Langmuir isotherm upon which it was based. The constant c may be generally approximated according to the relationship:

$$c = \exp((Q_1 - Q_v)/RT) \quad . \qquad (13)$$

The BET Equation 11 applies to infinite layers of adsorbed molecules. If adsorption is restricted to only n number of layers, the equation takes the form:

$$v = \left[\frac{v_m cx}{(1-x)}\right]\left[\frac{1-(n+1)\ x^n + nx^{n+1}}{1+(c-1)\ x - cx^{n+1}}\right] \tag{14}$$

Numerous investigators have assumed that the adsorbed phase behaves as a two-dimensional fluid on the solid surface, in that the motion of the adsorbate molecules is restricted to the plane of the adsorbed film on the solid surface. Such an approach, however, found only limited success, particularly in multimolecular adsorption. De Boer (2) has pointed out that adsorbate molecules may move from one site to another, not only by translational motions, but also by a desorption-adsorption mechanism at reversible equilibrium. The general approach has been to first determine the adsorbed-phase equation of state, if such could be found, and then attempt to derive the applicable adsorption isotherm by application of the Gibbs' equation:

$$\pi = (RT)/v_o \Sigma \int_o^P v\ d\ln P \quad , \tag{15}$$

where π is the two-dimensional film pressure corresponding to the three-dimensional pressure, P. Adamson (1) gives a good discussion of the numerous equations of state that have been used and the resulting related adsorption isotherms. The van der Waals type equations of state have been widely used. De Boer (2) used a two-dimensional van der Waals equation, but he pointed out that the van der Waals equation, and likewise the related adsorption isotherm, could not

satisfactorily describe the behavior of the adsorbate at high pressures, thus limiting the applicability of the technique.

Harkins and Jura (22) assumed the adsorbate to be a condensed film and proposed an equation of state from which, by applying the Gibb's relationship, there results the related adsorption isotherm:

$$\ln P/P_o = B - A/v^2 \tag{16}$$

where $$A = a\,\Sigma^2 v_o^2 / 2RT \tag{17}$$

and Σ is the area per gram expressed as:

$$\Sigma = k' A^{1/2} \tag{18}$$

where $$k' = (2RT / av_o^2)^{1/2} \quad . \tag{19}$$

For a proper fit of experimental data, a plot of $\ln P/P_o$ versus $1/v^2$ produces a straight line. The Harkins-Jura isotherm considers the adsorbed film to be monomolecular in nature.

In order to circumvent the inherent restriction of the de Boer treatment to the low-pressure region, Payne (31) used an equation of state derived by Eyring and Hirschfelder (9, 24) from a simplified cell model for liquids and derived an adsorption isotherm patterned after the treatment of de Boer using the Gibb's adsorption equation.

Payne experimentally measured the adsorption of methane and n-butane pure component gases on Columbia G charcoal at pressures to 2000 psi and temperatures from 0° to 90° C. A few methane-n-butane mixtures were also used, but were not correlated. The data were fitted to the derived isotherm equation by determining the best values of the empirical constant c that satisfied the following general isotherm equation:

$$f_3 = \frac{K}{(\alpha^{1/2} - cb_2^{1/2})^2} \exp\left[\frac{cb_2^{1/2}}{\alpha^{1/2} - cb_2^{1/2}} - \frac{2a_2}{RT\alpha}\right], \qquad (20)$$

where f_3 is the fugacity in a three-dimensional system, and α is the area of the adsorbent divided by the number of molecules adsorbed.

Payne's treatment is a semi-theoretical method of correlation, incorporating both empirical and theoretical considerations. The validity of the technique, due to the empirical nature of the fitting of the experimental data, does not seem to be fully substantiated as the underlying physical model of adsorption.

Although many equations of state have been proposed, and isotherm equations have been derived from them, this approach has not seemed to meet with full success in establishing the validity of the models proposed. As a matter of fact, Brunauer (3) has pointed out, and reasonably so it would seem, that the equation of state approach seems to be less fruitful to the interpretation of experimental data than does the use of adsorption isotherm equations. Brunauer further points out that "the isotherm equation contains only variables that can be readily measured, therefore its validity can be readily tested", whereas the equations of state generally contain surface area terms which can only be approximated and two-dimensionsal surface pressure terms which cannot be measured directly at all.

Other recent experimental data have been published by Walters (35) for the adsorption of light hydrocarbons on activated Columbia G charcoal. Ray and Box (32), likewise, reported the results of adsorption experiments on cocoanut charcoal in the pressure range of 0

to 215 psia and the temperature range of 100° to 450°F.

Some of the more useful adsorption equilibrium data were reported for both pure components and gas mixtures by Lewis, et al (27, 28, 29). Pressures ranged to 20 atmospheres, and the temperature ranged from 0° to 40°C. for the mixtures and up to 250°C. for the pure component isotherms. In both cases, the experimental data were correlated by a modification of the Polanyi (36) adsorption potential method, which is based upon the view that the adsorbent exerts a strong influence upon the gas molecules in the vicinity of the solid. The adsorption is the result of the forces of attraction involved. The adsorption potential is the greatest near the adsorbent surface and extends its attractive effects for several layers of adsorbate from the surface. In this treatment, the exact equation of state of the adsorbed phase is unknown, but it is assumed that the same equation of state applies to the adsorbed phase as to the equilibrium gas phase. The adsorption potential term may be expressed in the form:

$$(RT/V_i)\ln f^\circ_L/f^\circ_V \qquad (21)$$

where V_i = the molal volume of saturated liquid at the boiling point temperature corresponding to the adsorption pressure.

f°_L = the fugacity of the pure component as saturated liquid at the adsorption temperature.

f°_V = the fugacity of the pure component as vapor at the adsorption temperature and pressure.

Lewis' data (27, 28) for both silica gel and Columbia G carbon could be correlated with the Polanyi potential method quite well, but it was also found that the Langmuir, Freundlich, and BET theories could also be used to fit the data over a more limited pressure range for the pure components. The mixture data were correlated by the equation:

$$\sum_{1}^{n} N_1/N'_1 = 1 \quad . \tag{22}$$

The empirical correlation of Lewis also permitted the determination of the relative volatility, α', where

$$\alpha' = y_1x_2/y_2x_1 = P_1N_2/P_2N_1 \tag{23}$$

for binary mixtures.

Perhaps the most promising method of correlating experimental data and illuminating the physical model of adsorption lies in the development by Hill (23) for multimolecular adsorption from a mixture of gases. This development was a modification of the BET theory for pure component gases and postulated that the adsorption from a mixture of gases could be treated by assuming that the molecules of the second and subsequent layers have the "evaporation-condensation properties of a liquid mixture at the same temperature and composition". This development further assumed that the average energy of attachment of a gas molecule on any subsequent layer, i, was a function of the composition of the (i - 1)th layer only. The resulting adsorption isotherm for n numbers of layers was:

$$v_i/v_{mi} = \Big\{ E_o \Big[(1 + E_1 + E_1E_2 + \ldots + E_1E_2 \ldots E_{n-1})\ \gamma_{i1} + (E_1 + \ldots + E_1E_2 \ldots E_{n-1})\ \gamma_{i2} + \ldots \ldots E_1 \ldots E_{n-1}\ \gamma_{in} \Big] \Big\} \Big/ \Big\{ 1 + E_o\ (1 + E_1 + E_1E_2 + \ldots + E_1E_2 \ldots E_{n-1}) \Big\} \qquad (24)$$

where $E_o = \sum_i x'_i Q_i$ (25)

$$E_j = x'_1 f_1(N_j) + x'_2 f_2(N_j) + \ldots,\ j = 1,2, \ldots \qquad (26)$$

$$x'_i = P_i/P^o_i \qquad (27)$$

$$N_{i1} = x'_i Q_i/E_o \qquad (28)$$

$$N_{ij} = x'_i f_i(N_{j-1})/E_{j-1} \qquad j = 2,3, \ldots \qquad (29)$$

$$\gamma_1 = N_1 / \Big[(N_1 + N_2\ (v^o_2/v^o_1)^{2/3} + N_3\ (v^o_3/v^o_1)^{2/3} + \ldots) \Big] \qquad (30)$$

$$Q_1 = \exp\ \Big[(q_1 - q_{11})/RT\Big]$$
$$Q_2 = \exp\ \Big[(q_2 - q_{22})/RT\Big] \qquad (31)$$

where q_i = heat of adsorption per mole of i on the bare surface of the solid.

q_{ii} = heat of adsorption per mole of i on a layer of pure i.

Similar expressions for γ and Q can be written for each component on each subsequent layer.

Since the development of these equations by Hill, little experimental data have been obtained with which the theory could be properly tested. Only recently, Mason and Cooke (30) reported the results of adsorption experiments of light hydrocarbons from methane to hexane on silica gel. Both pure components and mixtures with methane were used over a pressure range to 1800 psia. Most data were reported for 100°F. In order to correlate the experimental data to account for the non-ideality of the gas phase, Mason and Cooke modified the treatment of Hill to incorporate fugacities of vapor phase components instead of the usual pressure terms. Both the Langmuir and Polanyi potential theories of adsorption were found unsatisfactory as tested by Mason and Cooke. However, as will be discussed in a later chapter, there is some question as to the validity of the calculation procedure used by Mason and Cooke in their mixture experiments. Pure component adsorptions were calculated by the standard BET equation in the form:

$$f/v(f^o - f) = 1/cv_m + (c-1)(f/f^o)/cv_m \tag{32}$$

Plots of $f/v(f^o-f)$ versus f/f^o allowed the determination of the BET energy constants c and v_m for the pure component gases.

The BET equation for adsorption from mixtures of gases was taken from Hill. For two layer adsorption it may be expressed as:

$$v_i/v_{mi} = E_o \left[(1 + E_1)\ \gamma_{i1} + E_1\ (\gamma_{i2})\right] \Big/ \left[1 + + E_o\ (1 + E_1)\right] \tag{33}$$

where

$$E_o = \sum_{i=1}^{n} x'_i c_i \tag{34}$$

$$x'_1 = f_i/f^o_i \tag{35}$$

$$E_1 = \sum_{i=1}^{n} x'_i f_i\ (N_{i1}) \tag{36}$$

$$F_i(N_{i1}) = N_{i1}\ f^o_i/f_{L_{i1}} \tag{37}$$

$$N_{i1} = x'_i c_i/E_o \tag{38}$$

$$\gamma_{ij} = N_{ij}/\ \left[N_{1j}\ (A_1/A_i) + N_{2j}\ (A_2/A_i) + \ldots + \right.$$

$$\left. + N_{nj}\ (A_n/A_i) \right] \tag{39}$$

$$N_{i2} = x'_i F_i\ (N_{i1})/E_1 \tag{40}$$

The term $F_i(N_{i1})$ of Equation 36, according to Mason and Cooke, corrects for deviations from ideal solution behavior in the adsorbed phase. The Benedict-Webb-Rubin equation of state for light hydrocarbons (14) was used in the fugacity calculations.

Another mixture equation was presented by Tryhorn and Wyatt (34) in their investigation of the adsorption of binary gas mixtures on charcoal. For binary mixtures,

$$\mu_1/\mu_2 = P_1 M^{1/2}{}_2/P_2 M^{1/2}{}_1 \tag{41}$$

where P_1 and P_2 are partial pressures of components 1 and 2, respectively; M_1 and M_2 are molecular weights, and μ_1 and μ_2 are the respective numbers of molecules striking the surface per second and are given by:

$$\mu = PS/(2\pi MRT)^{1/2} \tag{42}$$

where S is the surface of the adsorbent.

The study and understanding of the principles involved in mixed adsorption is very important, because most commercial applications involve more than single component adsorption processes. The theoretical treatment of mixed adsorption, however, is much more difficult than that of adsorption of pure component gases. It seems that any useful correlation or prediction technique for mixture adsorption must be able to predict the amount of component adsorbed and, at the same time, define satisfactorily the vapor-adsorbate equilibrium relationships involved.

To date, there have been many attempts to theoretically and/or experimentally describe the adsorption phenomenon occurring, and, as the literature review has revealed, there has been a tendency in the past to take the equation-of-state approach in correlating experimental data. The adsorption isotherms derived from these equations-of-state have been semi-empirical in nature and have not seemed to be satisfactory in describing the adsorption process, particularly in those systems involving mixtures of gases. Very little pertinent information on adsorption from gas mixtures has been published.

The literature survey has shown the importance and need for good reliable adsorption equilibrium data on hydrocarbon gas mixtures, from which useful and meaningful prediction methods for design purposes may be drawn. Thus, the primary objective of this study was to provide such equilibrium data and to determine the most useful model for predicting adsorption isotherms and for clarifying the factors governing equilibrium adsorption behavior.

The determination and presentation of such information, along with a definition of the underlying physical model of adsorption, would

constitute a major contribution to the technology and understanding of adsorption processes in the petroleum industry.

CHAPTER III

EXPERIMENTAL APPARATUS AND MATERIALS

A schematic drawing of the basic experimental adsorption apparatus is shown in Figure 1. The apparatus was designed to operate at constant adsorption temperature and pressures to 1800 psig. The system was essentially a volumetric system in which the amount of gas injected, displaced, and remaining in the adsorption cell could be determined from PVT calculations and chromatographic gas analyses.

The gas injection system consisted of a motor-driven mercury injection pump, a stainless steel PVT mixture transfer cell, and a Heise pressure gauge calibrated by a dead weight tester. The PVT cell was constructed to permit rocking the cell to facilitate gas mixing prior to commencement of an adsorption run. An attempt was made to operate the PVT cell with a temperature controlled heating jacket, but the procedure was discarded when it would not permit rocking the PVT cell during gas make-up. Actually, the jacket was not needed after all, inasmuch as the injection gas temperature never varied by more than $\pm$ 0.5° F. during the relatively short period of time required for injection of the gas sample into the cell. Stainless steel tubing and fittings were used throughout the system.

The adsorption cell was a Hoke high-pressure stainless steel cylinder with an internal volume of about 30 cubic centimeters,

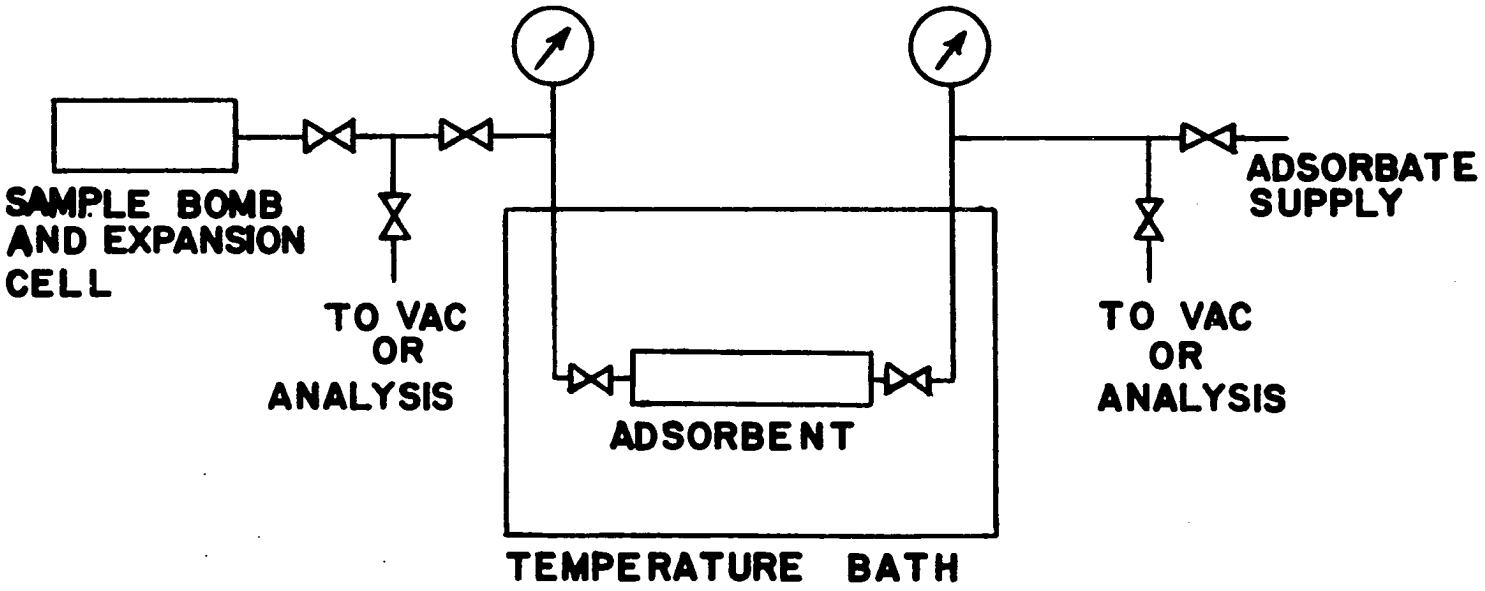

FIGURE I SCHEMATIC DIAGRAM OF APPARATUS

designed for service to 1800 psi. Each end of the cell was provided with a stainless steel needle valve. The adsorbent used in these experiments was Davison Chemical Company's 03 grade, 3-8 mesh, silica gel. A single sample of the gel was selected, heated, evacuated, and weighed before packing it into the adsorption cell. The same single sample of gel was used throughout all the experiments in order to remove any extraneous effects of varying gel properties. The sample of gel used weighed a total of 19.64 grams when heated and evacuated. Small plugs of steel wool and fiber glass were placed at each end of the adsorption cell to help hold the adsorbent in place and to prevent any adsorbent dust from getting into the needle valve seats. Stainless steel fittings were also used on the adsorption cell.

The temperature of the adsorption cell was controlled during a given run by placing it in a temperature controlled water bath at 100° F. The temperature variation of the bath never exceeded more than about $\pm$ 0.5° F. during the course of any adsorption-desorption experiment.

Another calibrated pressure gauge was connected to the downstream side of the adsorption cell to provide pressure experiments during the desorption runs. Any displaced gases were collected in another Hoke high-pressure cylinder connected to the outlet end of the adsorption cell. This cylinder served as an expansion cell for the desorption runs as well as a sample container from which the displaced gas could be analyzed with the chromatograph.

Adsorption cell weights were measured with an O'Haus balance capable of weighing the entire adsorption cell to within 0.01 grams.

It was demonstrated in the calculations that errors in measurements of $\pm$ 0.01 grams had no significant effect upon the calculated results of the experiments. Thus, more accurate weights were not justified nor necessary in these experiments.

A mercury pump capable of producing a vacuum of 0.1 microns absolute pressure, or better, was used in all of the experimental runs when evacuations were required. A high-temperature oven provided the heat required, in conjunction with the mercury pump, for regeneration of the adsorbent after each adsorption-desorption experiment.

The methane, n-butane, n-pentane, and n-hexane hydrocarbon components used in the experiments were all Phillips Pure Grade components with a guaranteed 99 mol per cent minimum analysis. Phillips Reference Standard Gas #7, according to the NGAA recommended procedure for chromatographic gas analyses, was used as the basis of calculating all gas analyses.

Inasmuch as no suitable chromatographic unit was available at the University at the time these experiments were conducted, it was necessary to construct an operable chromatograph from commercially available components. A Gow Mac Instruments Company Model TR III-A Temperature Controlled Cell was used to house a Gow Mac #9285-Pretzel Type hot wire thermal conductivity cell detector, using Tungsten W-2 matched filament detectors in both the reference and sample passes. A Gow Mac Model 9999 Power Supply Control Unit provided controlled current to the detector elements and provided suitable attenuation of sample signals to the Honeywell Brown Electronik one-millivolt recorder. Pure, dry helium was used as the carrier and reference gas for

all analyses. The sample valve was a four-way Circle-Seal valve into which was built a sample loop of 1/8-inch stainless steel tubing of unknown volume, but estimated to be of the order of 0.5 cubic centimeters internal volume. Actually, accurate determinations of the sample loop size was unnecessary since all samples were admitted into the evacuated sample loop at less than atmospheric pressure, and reference gases were taken at the same pressures for direct comparison and calculation of gas composition. Several chromatographic columns, depending upon the components being tested, were used. In the n-butane runs, a 15-foot column of 30 weight per cent HMPA on 100/120 mesh firebrick was employed for satisfactory separations of the hydrocarbon components. For n-pentane and n-hexane a 5-foot column of 25 weight per cent of an ether compound on 42/60 mesh acid-washed Chromasorb (firebrick) was used for suitable separations. Sample carrier gas flow rates and operating temperatures were adjusted to give separations within 8 to 10 minutes from injection of the sample into the analyzer. Brooks Instrument Company "Sho-Rate 150" flow controllers were used on the carrier and reference gas streams to maintain nearly constant flow rates of helium through the detectors. A Hoke metering valve admitted the gas sample to the sample loop. The system was constructed such that any or all parts of the system could be evacuated before any gas sample was to be analyzed.

CHAPTER IV

EXPERIMENTAL PROCEDURE

After the equipment had been constructed and prior to commencement of any adsorption tests, the "dead volume" or empty space within the adsorption cell was determined by pressuring the cell with helium to a known pressure, at known temperature. The cell was then bled off to atmospheric pressure and the volume of helium so displaced was measured by water displacement in a gas burette. Several measurements were taken also by measuring the helium with a wet test meter. The volume of the empty space within the cell was thus calculated from PVT considerations to be 21.27 cubic centimeters. Helium compressibility factors were taken from Canfield (17).

Injection gas samples were made up by first evacuating the PVT cell, admitting a predetermined quantity of the heavier hydrocarbon component to give a desired concentration, and then pressuring to 1000 psig with pure methane gas. The sample was then rocked in the PVT cell, containing some mercury, to facilitate mixing. The exact composition of the injection gas was then determined by chromatographic analysis. At least three samples were analyzed, and the average value was taken.

The adsorption cell was prepared for a given run by placing it in the oven at 400° F. overnight. The cell was continually evacuated

during the heating process. Just prior to commencement of an adsorption experiment the dry, evacuated cell was weighed. The adsorption cell, after cooling to near room temperature, was then placed in the 100° F. water bath and allowed to come to equilibrium with the bath temperature. A short stainless steel 1/8-inch line was then connected from the PVT transfer cell to the adsorption cell and evacuated. The needle valve at the inlet end of the adsorption cell was then opened slightly, and the gas mixture was injected, at constant pressure of 1000 psig, by means of the mercury pump. Mercury pump readings were recorded to afford a means of calculating the number of moles of gas mixture injected into the adsorption cell. After a pseudo-equilibrium had been reached at 1000 psig, the outlet needle valve on the adsorption cell was cracked and gas was displaced through the cell at a very slow rate, maintaining a constant pressure of 1000 psig until several pore volumes of gas had been displaced through the cell. The displaced gas was collected and analyzed by the chromatograph. The cell was shut in and allowed sufficient time to reach a good equilibrium at the 1000 psig level at the bath temperature of 100° F. All adsorption runs had this initial adsorption step at 1000 psig. After equilibrium had been reached, a small gas sample (at a few millimeters of mercury absolute pressure) was drawn off the adsorption cell dead volume and analyzed by the chromatograph to give the equilibrium gas phase composition in the adsorption cell. Thus, each run required three different gas analyses, viz., that of the injection gas, equilibrium gas, and the displaced gas. The adsorption cell was then removed from the system and the weight of the cell was again recorded, so that the

weight of each component adsorbed on the silica gel could be calculated from a material balance on the amount injected, amount displaced, and amount remaining in the adsorption cell dead volume. This procedure essentially consisted of the injection of a measured quantity of gas of known composition into the adsorption cell, and the resulting equilibrium conditions were then examined and determined. The injection gas in all cases had a higher concentration of heavier component than the equilibrium gas composition. This technique was very flexible in that the exact amount of material adsorbed could be measured after the injection of any given quantity of gas. Thus, if after one series of injections the equilibrium gas phase concentration had not reached the desired level, the cell could be placed again in the system and more gas injected, of course keeping close account of all materials injected or displaced, until the equilibrium gas concentration was near the desired level. Actually, an entire isotherm over a wide range of gas compositions could be determined in this manner for any desired pressure level.

After the desired equilibrium had been reached at 1000 psig, the sample collection system was evacuated up to the outlet needle valve on the adsorption cell. The adsorption cell was then opened to the expansion cylinder and downstream pressure gauge so that the adsorbed phase could "flash" off the gel, expand into the cylinder, and reach a new lower equilibrium pressure level. This desorption procedure was used for all pressures less than 1000 psig. After allowing sufficient time for equilibrium temperature and pressure to be reached, generally 30 minutes or more, the displaced gas and dead volume gas were again

analyzed to determine the composition. The cell was again removed from the system and weighed on the balance. Then, from a knowledge of the amount of each component adsorbed at the previous equilibrium level, and the amounts of gases remaining in the cell dead volume and displaced from the cell upon desorption, the quantity of each component adsorbed on the silica gel at the new equilibrium pressure level could be determined by material balance calculations. This technique of desorption was repeated until a wide range of equilibrium pressures had been determined. The technique allowed the determination of much more adsorption data than could have been obtained by strictly adsorption techniques in the same amount of time allotted. The literature further suggested that desorption hysteresis effects would not be significant.

In order to verify the technique outlined above, one run, number 7, was conducted in a different manner by flowing the injection gas through the adsorption cell at very low flow rates until the exit gas concentration was the same as the inlet injection gas concentration. The adsorption so calculated can be seen in Figure 11 to be in excellent agreement with the other data. Thus, the experimental procedure outlined above was verified as sound, and any doubts as to whether a true equilibrium had been reached at the measured composition, with this technique, were erased.

After a series of desorption pressure levels had been obtained, from 5 to 7 levels for each run, the adsorption cell was removed from the system, placed in the oven at 400° F. and regenerated by evacuating the cell overnight. It should be pointed out here that after

run 6, a somewhat different regeneration technique was employed as a check on the previous regeneration procedure. The adsorption cell was first evacuated cold, placed in the oven under vacuum and heated to 400° F. for one hour. The cell was then opened to the oven air and hot dry air was allowed to enter the cell. The cell was then shut-in again and evacuated at the 400° F. level overnight. The cell was again cooled to room temperature before being placed into the water bath. No differences in the two regeneration techniques were observed.

The last series of 3 runs were ternary gas mixtures, for which adsorption was determined at the 1000 psig level in the same manner as for the binary runs. Two lower equilibrium pressures were obtained by a similar desorption process described above. The only differences involved were in the complications introduced by the mere addition of another component. The experimental technique, analysis, and calculation procedure was the same as for the binary mixtures.

The experimental apparatus was not at all complicated, save for the construction of the chromatograph unit. The experimental procedure, while somewhat time-consuming, was rather simple and allowed more rapid determination of adsorption data than would normal adsorption techniques.

CHAPTER V

RESULTS AND DISCUSSION

The experimental and calculated results are presented in Figures 3-41 and Tables 1-16. Typical run data are shown for illustration purposes in Figures 2, 3, and 4.

At the outset of these experiments, it was surmised, without any really theoretical basis at the time, that adsorption of the heavier hydrocarbon components inside the primarily 21 angstrom pores of the 03 grade silica gel could not physically extend beyond the monolayer region. It was thus believed that the ultimate correlation of the experimental data might well be satisfactorily handled by one of the monolayer theories of adsorption.

Pore Size Restriction on Adsorption

Figure 5 illustrates an idealized pore system drawn to scale for a pore diameter of 21 angstrom units. Inside are pictured n-butane molecules with a diameter of 4.9 angstrom units, as calculated from Hirschfelder (9). This figure indicates, ideally of course, that adsorption inside the pores of the silica gel cannot physically be much more than one monolayer in thickness. When it is realized that the actual pore structure may be less than the spherical pores so pictured, it is easily seen that the hypothesis of monolayer adsorption is not

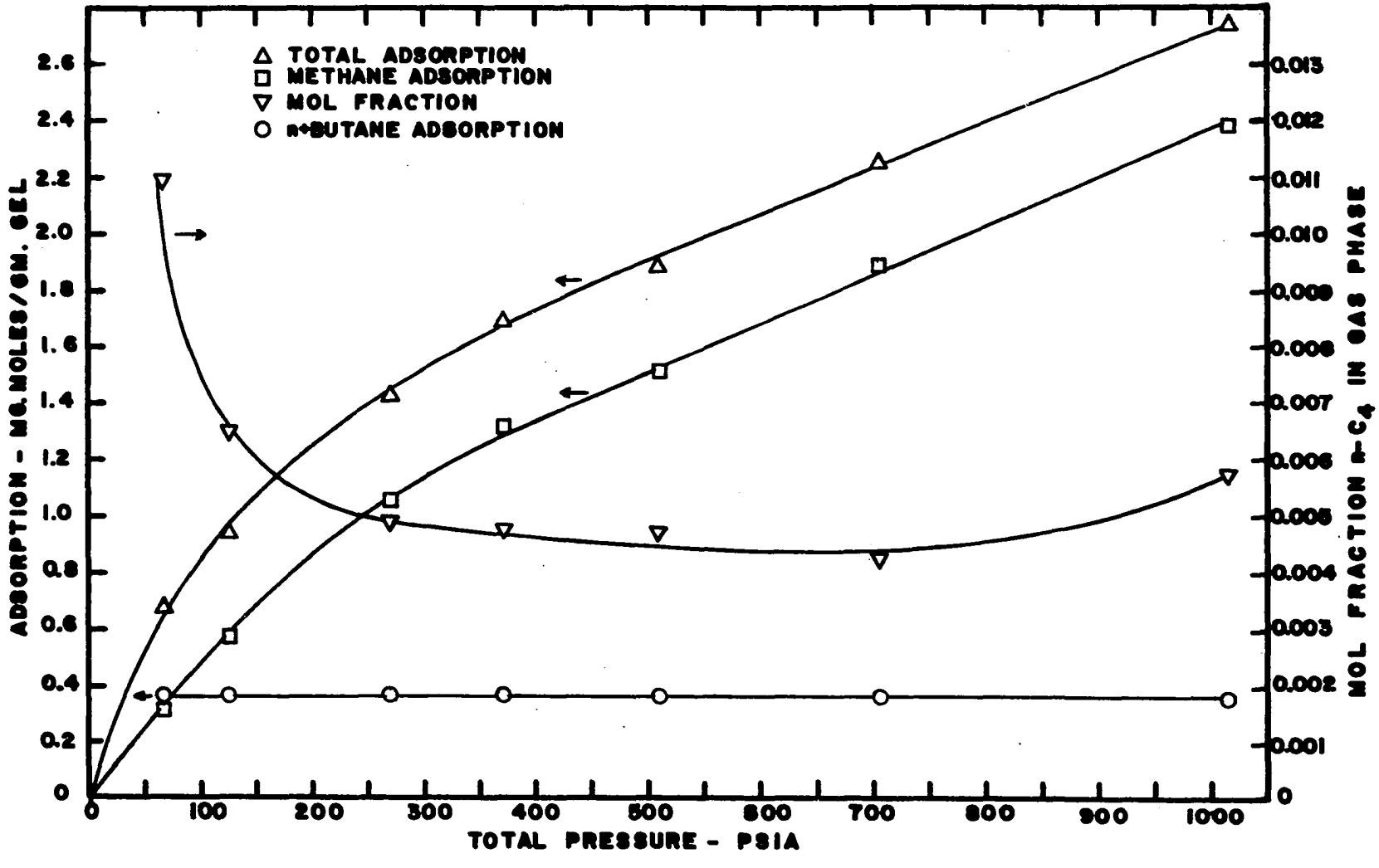

FIGURE 2 PRIMARY ADSORPTION DATA, RUN 3, $C_1 - nC_4$ MIX

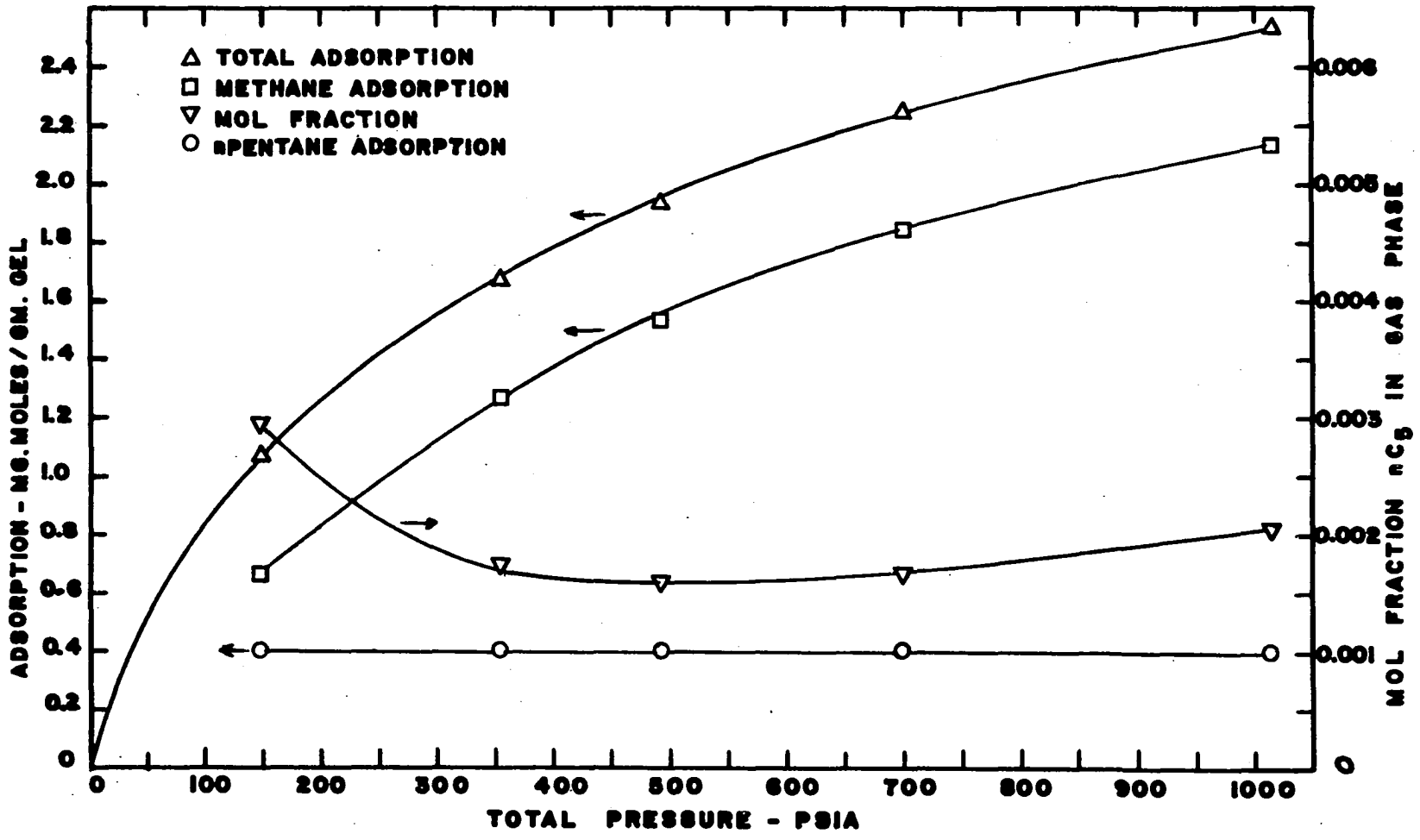

FIGURE 3 PRIMARY ADSORPTION DATA, RUN 10, C_1 - nC_5 MIX

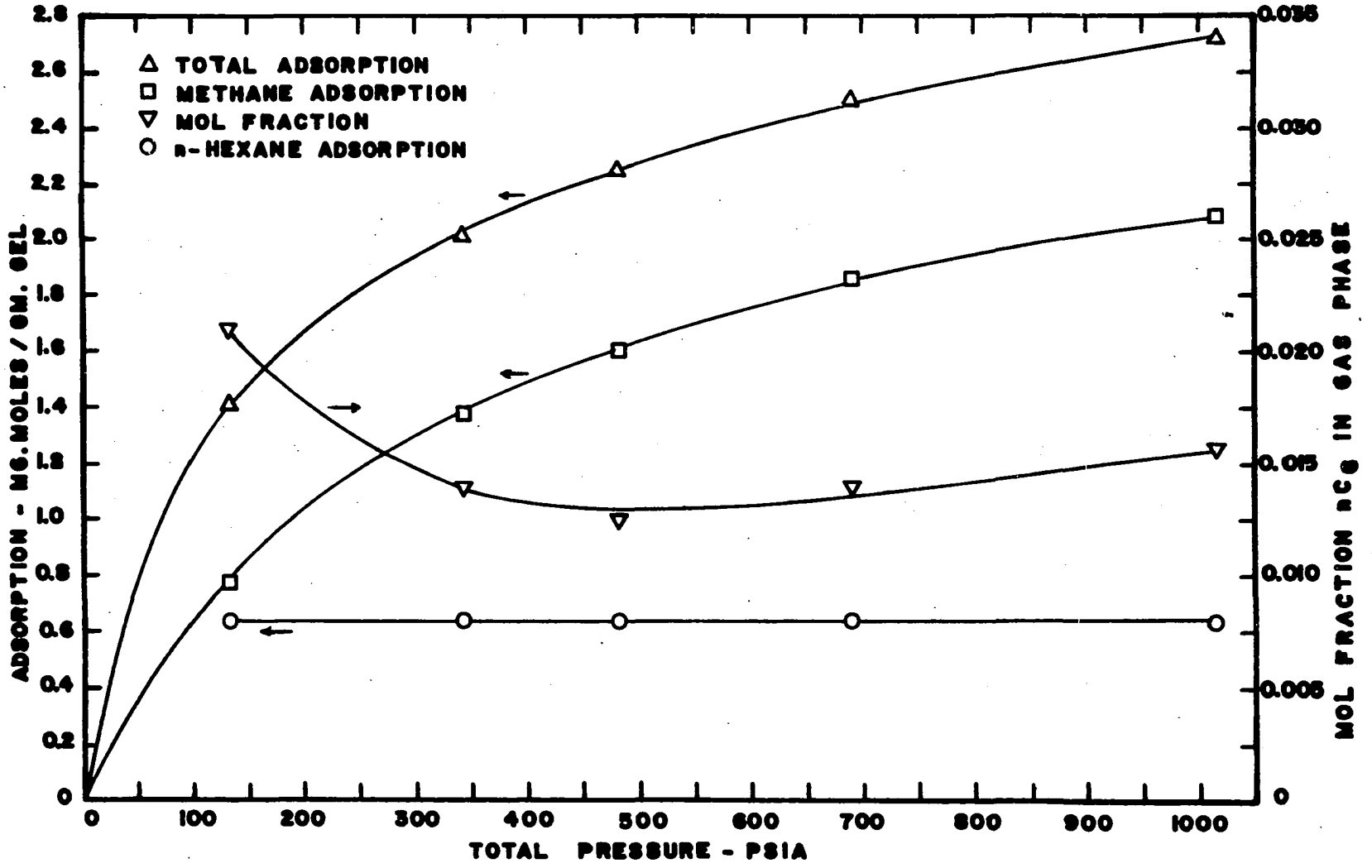

FIGURE 4 PRIMARY ADSORPTION DATA, RUN 12, $C_1 - nC_6$ MIX

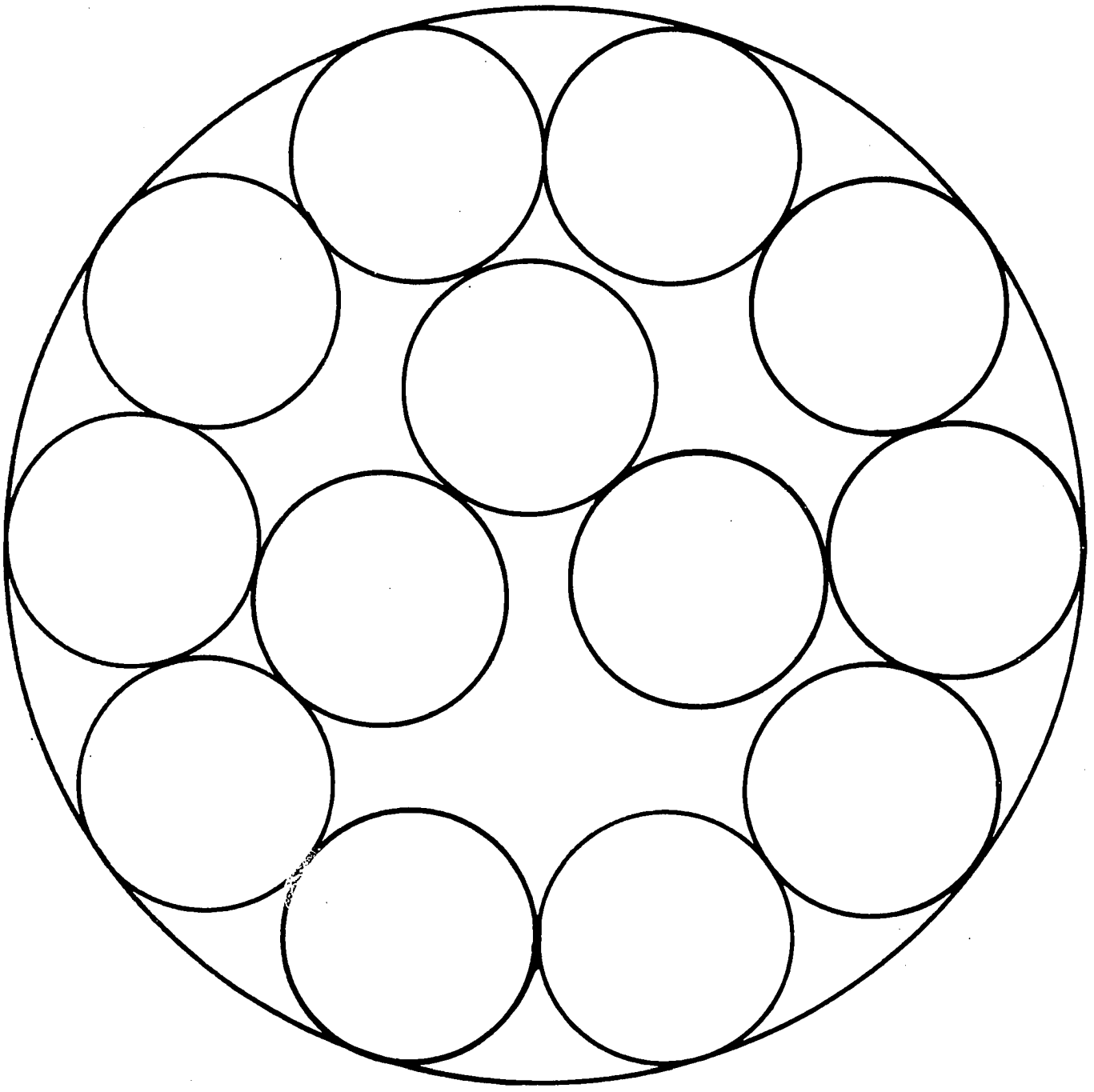

FIGURE 5 IDEALIZED ILLUSTRATION OF n-BUTANE MOLECULES ADSORBED INSIDE A SILICA GEL PORE

at all unreasonable. A similar comparison and illustration with the larger n-pentane and n-hexane molecules would further substantiate the hypothesis, because if n-butane adsorption is limited to monolayer coverage, then surely the adsorption of the larger n-pentane and n-hexane molecules must be limited by pore size restrictions. While it is admitted that some multilayer adsorption may occur on the outside surfaces of the gel in the pores between the individual gel particles, the bulk of the large reported surface area of the 03 gel (about 750-830 meter^2/gram), and accordingly the bulk of the adsorption, occurs in the capillaries contained within the individual gel particles.

Langmuir Isotherms

The experimental results were first checked by the Langmuir Equation 10 for mixture adsorption:

$$\theta_1/\theta_2 = K' P_1/P_2 \tag{10}$$

which may be expressed in the alternative form:

$$v_1/v_2 = K'' P_1/P_2 \tag{43}$$

where v_1 and v_2 are milligram-moles of components 1 and 2 adsorbed per gram of gel, and P_1 and P_2 are the partial pressures of the components. The experimental results, when plotted as v_1/v_2 versus P_1/P_2 (as shown in Figure 6) do, indeed, plot a straight line through the origin, as suggested by Equation 43. Thus, it was further concluded, in developing a suitable correlation technique, that the data may be

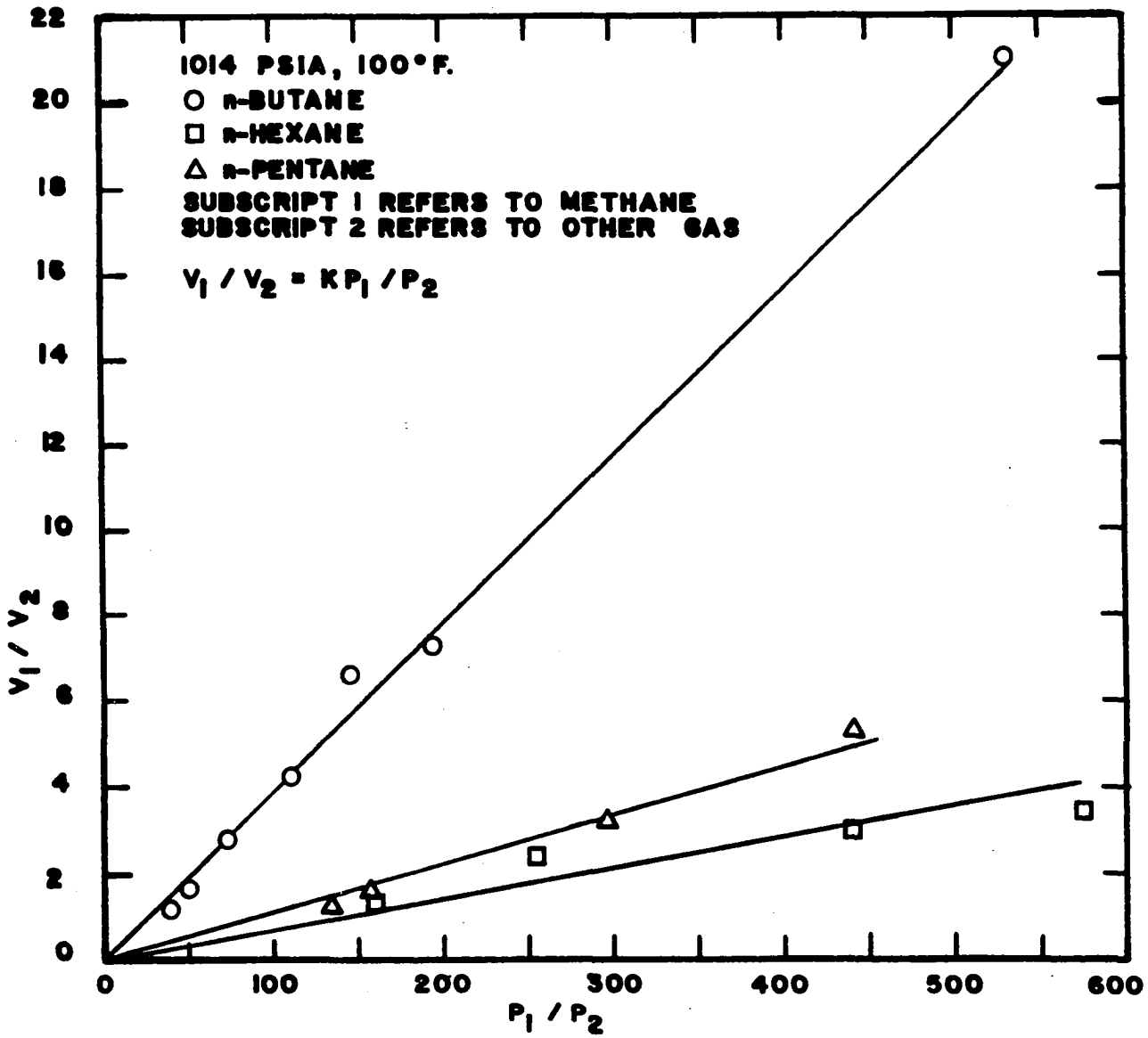

FIGURE 6 LANGMUIR ISOTHERMS

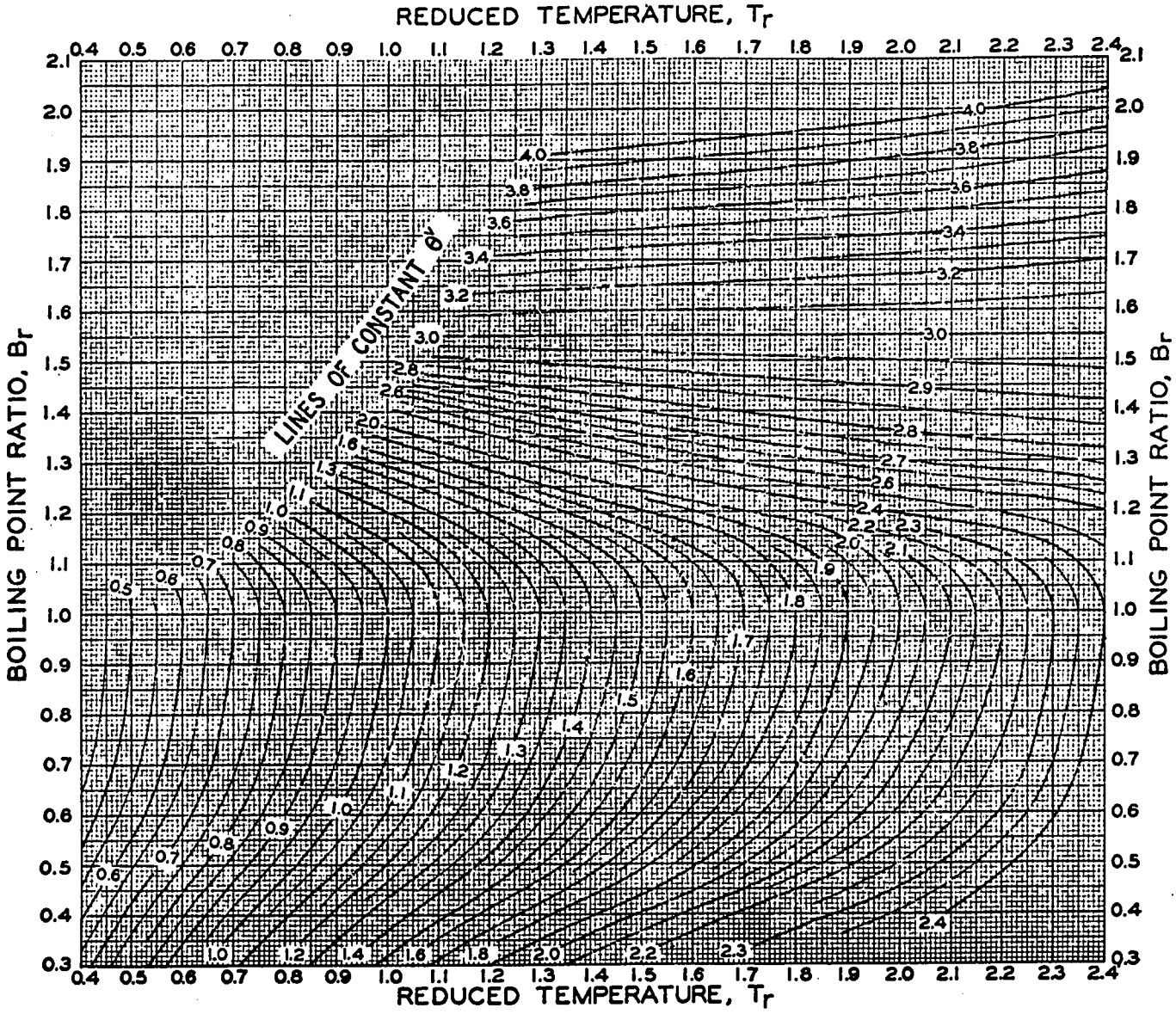

FIG. 7-Generalized temperature - composition function for hydrocarbon vapors (References 5, 19)

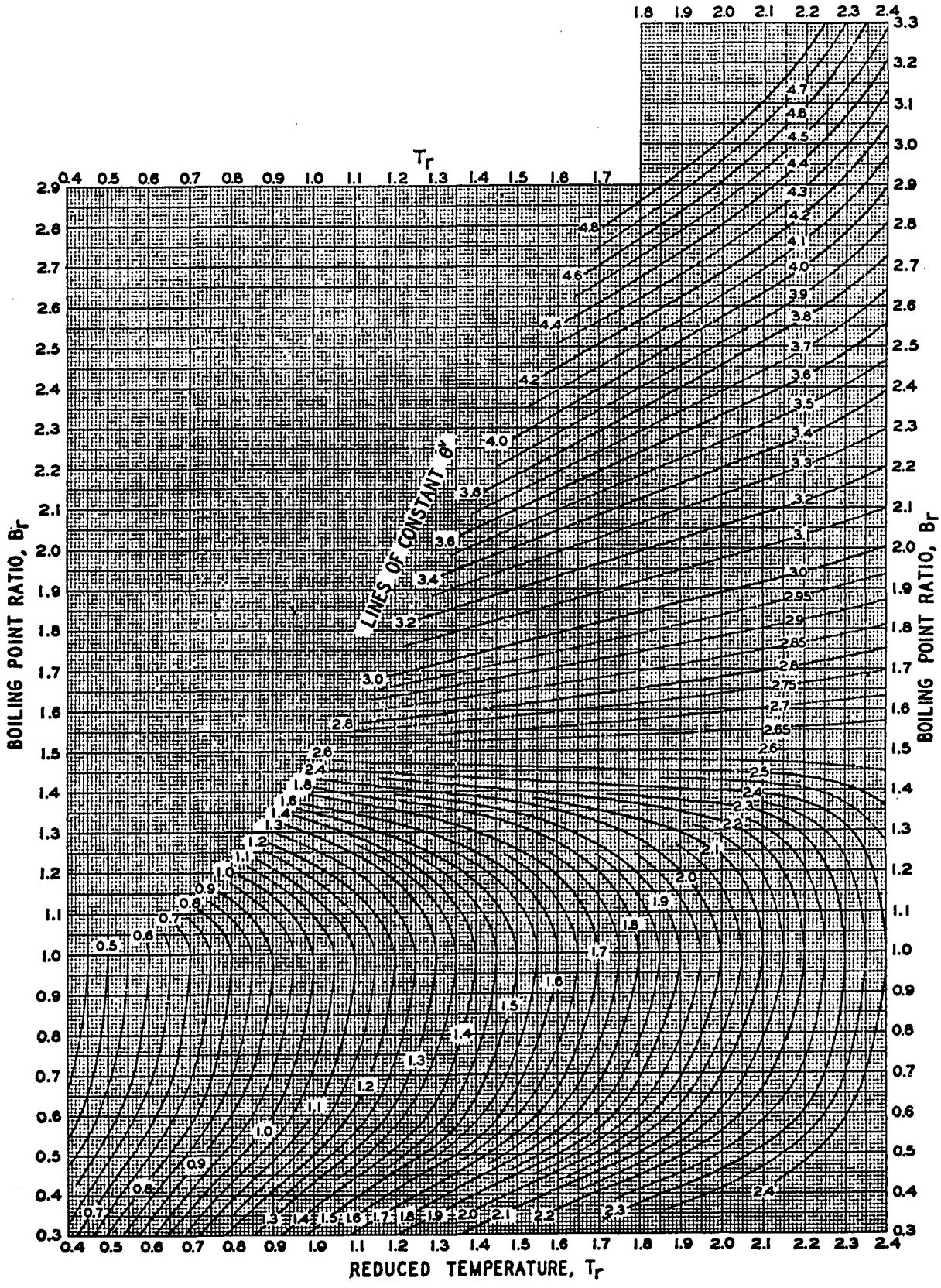

FIG. 8-Generalized temperature - composition function for methane vapor (References 5, 19).

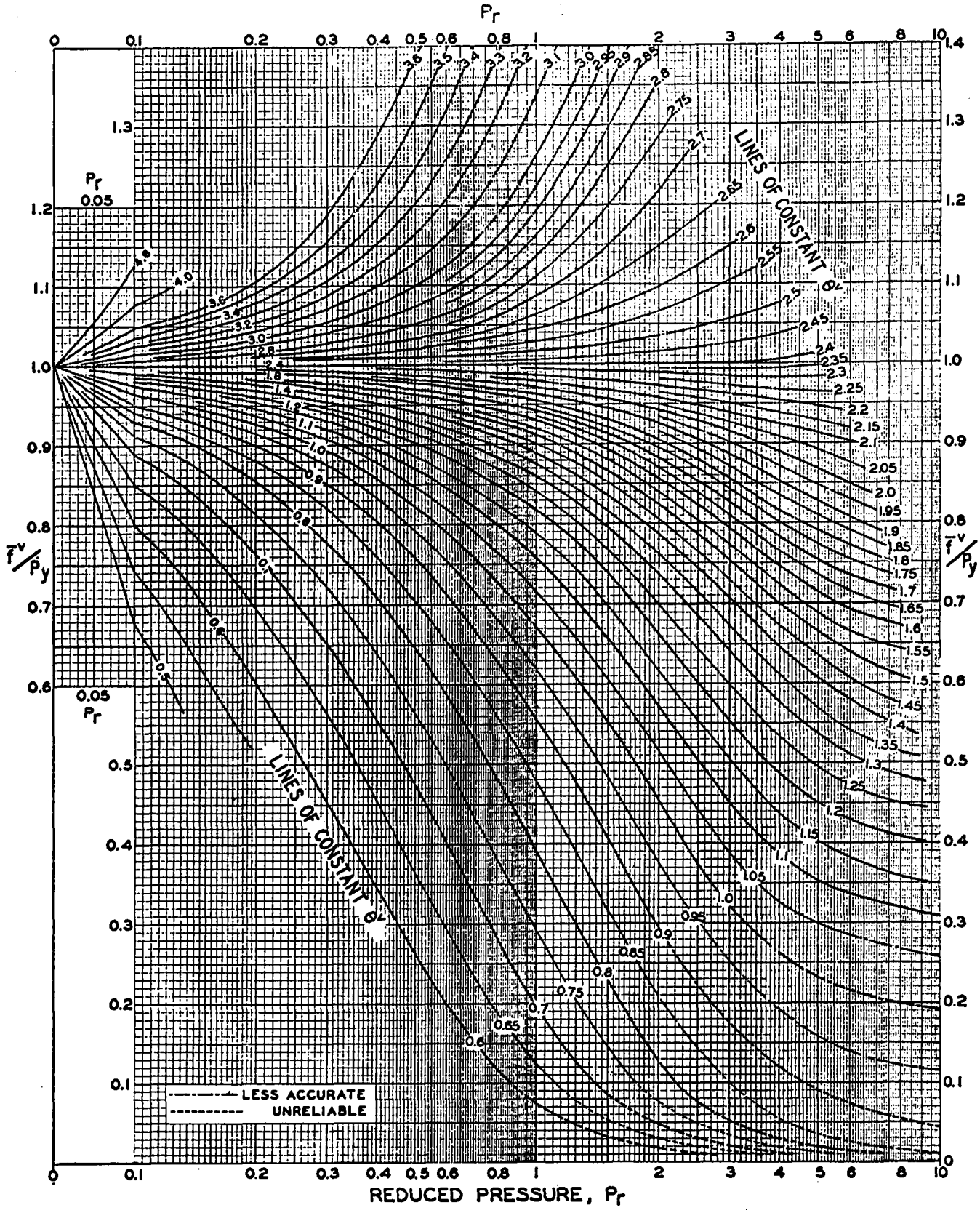

FIG. 9-Generalized fugacity coefficients for vapor mixtures(References 5, 19)

reasonably correlated by monolayer considerations, since multilayer adsorption did not appear to be significant.

Comparison of Experimental and Predicted Results

Inasmuch as the previous considerations very strongly indicated the existence of monolayer adsorption in the present work on gas mixtures, the calculation procedure outlined by Mason and Cooke (30), utilizing a modified form of Hill's BET treatment, was re-written for the case of only one layer of adsorption, where n = 1, resulting in the following BET monolayer isotherm, which necessarily is identical with the Langmuir isotherm from which it was derived. The amount of material adsorbed may be expressed by the equation:

$$v_i/v_{mi} = E_o \gamma_{il}/ (1 + E_o) \quad . \tag{44}$$

This equation may be obtained directly from Hill's equation for the case of n = 1. The terms E_o and γ_{il} are the same as defined by Mason and Cooke and presented in Chapter II.

The pure component data of Mason and Cooke (30) were used to evaluate the BET energy constants, c and v_m, for each pure hydrocarbon component. These values, as well as the values of f°, the pure component fugacity corresponding to the saturation vapor pressure, are tabulated in Table 1 and may be used in future calculations and predictions of mixture adsorptions.

The values of fugacities used in the calculations in the present work were obtained from the Edmister and Ruby charts (5, 19), reproduced as Figures 7, 8, and 9, which, in turn, were obtained from the Benedict-Webb-Rubin fugacity equation (14). The values so calculated

for the BET monolayer adsorption in binary mixtures are summarized in Tables 11-16. The results are plotted along with the experimental results, for comparison purposes, in Figures 10-28. These results show remarkably good agreement between the experimental results and the values predicted by the fugacity-corrected monolayer Equation 44, at all pressure levels and compositions used in the experiments. In most cases, the experimental values were slightly higher than the predicted values, particularly for the n-hexane isotherms. None of the deviations, however, is significantly large. The deviations, particularly in the n-hexane case, could possibly be due to some small amount of hysteresis in the desorption tests , although insufficient information is available to determine this exactly. It does not seem important, though, considering the extremely good fit between the experimental and predicted results.

Comparison of Theoretical and Experimental Bet Constants

It is interesting to point out here that the values of v_m reported by Mason and Cooke were for a reported 830 m^2/gm surface area gel, while the surface area of the gel used in these experiments was about 760 m^2/gm, as determined from actual laboratory measurement. A value of 800 $m^2/gram$, believed to represent an average value over the range reported, was used in the calculations in this study. When the Mason and Cooke values are reduced to units of milligram-moles per square meter of surface area, the resulting v_m values for the present gel becomes, for the adsorption of n-butane:

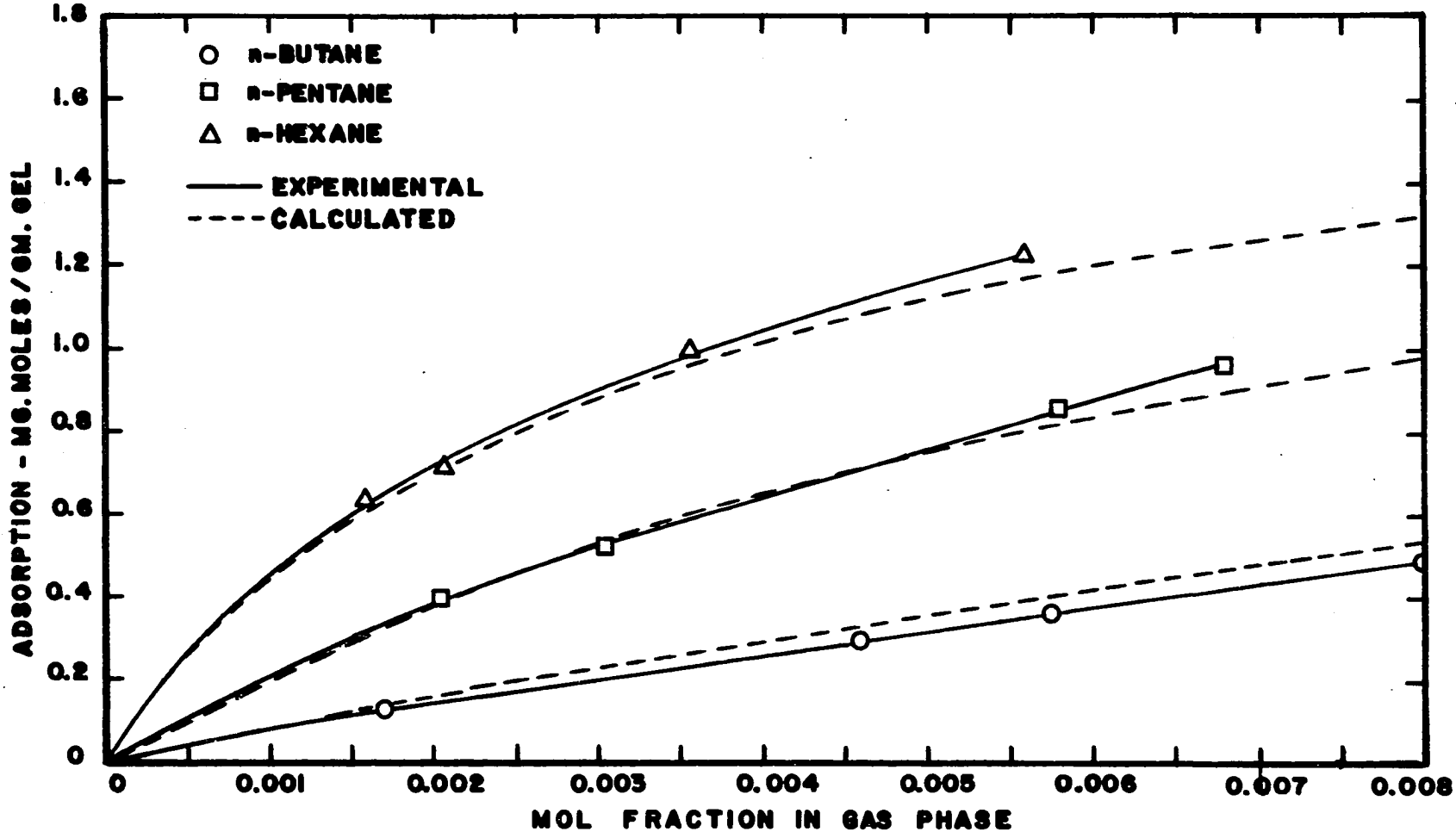

FIGURE 10 ADSORPTION FROM BINARY MIXTURES WITH METHANE, 1014 PSIA, 100°F.

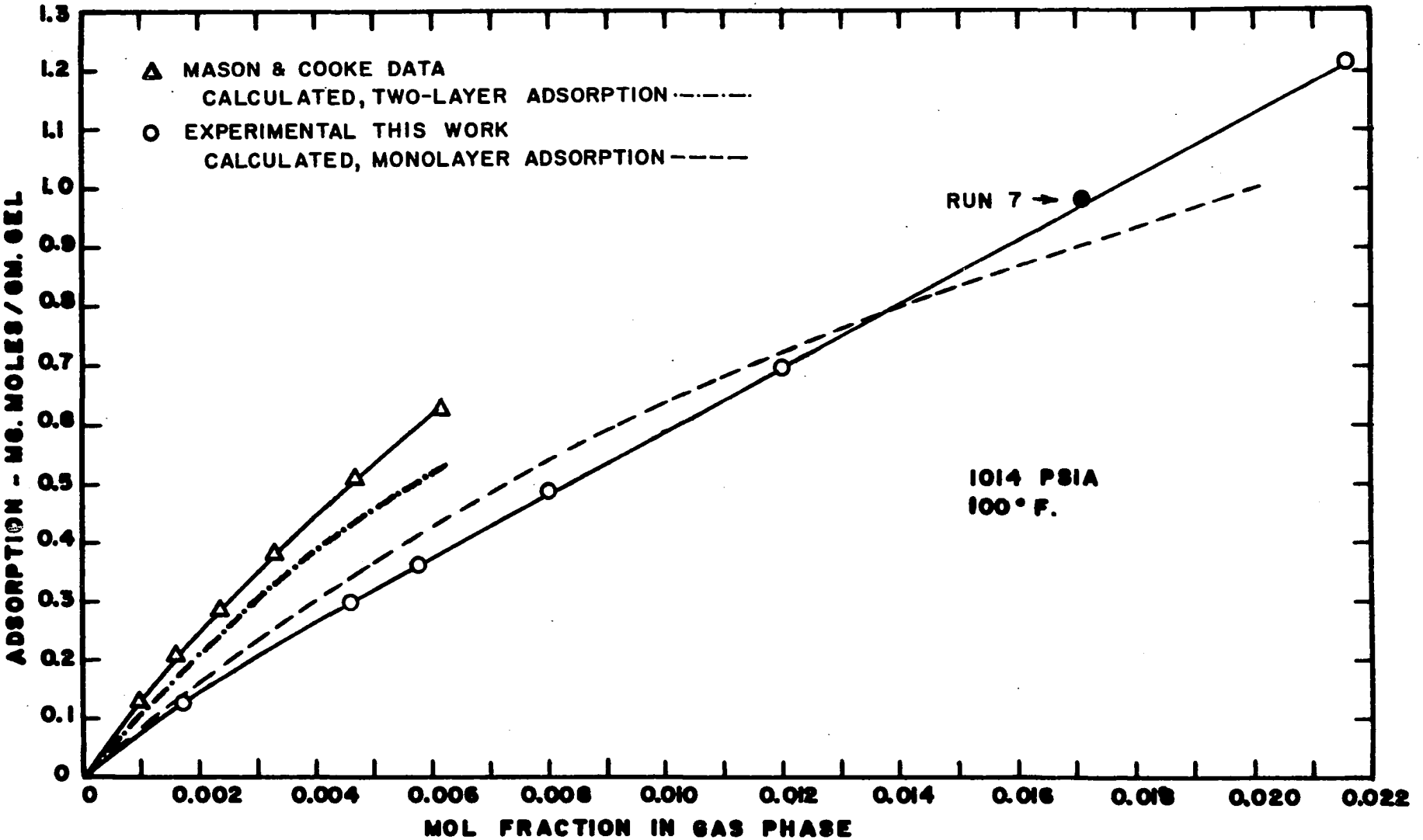

FIGURE 11 EFFECT OF CONCENTRATION ON nBUTANE ADSORPTION FROM METHANE - nBUTANE MIXTURES

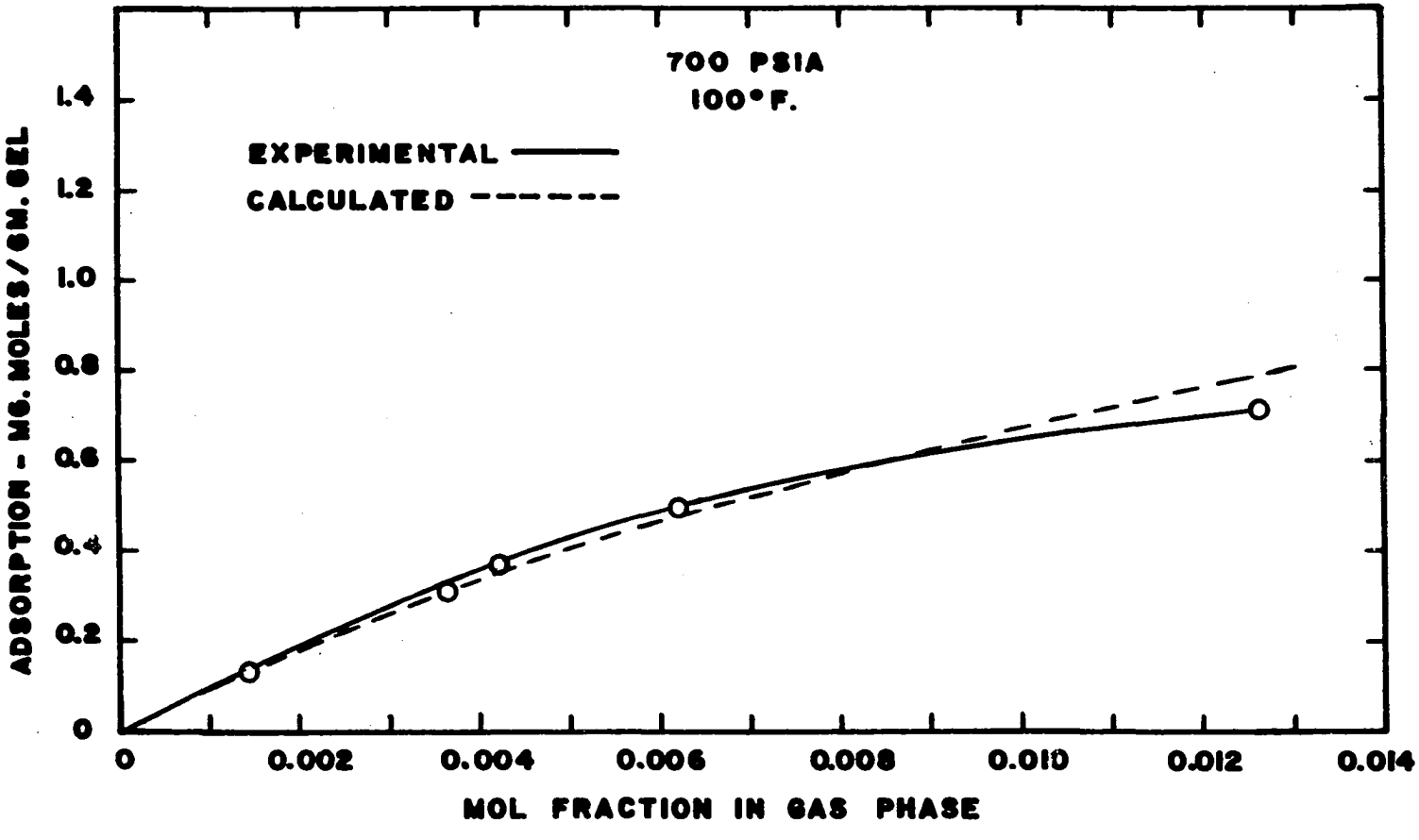

FIGURE 12 EFFECT OF CONCENTRATION ON nBUTANE ADSORPTION FROM METHANE - nBUTANE MIXTURES

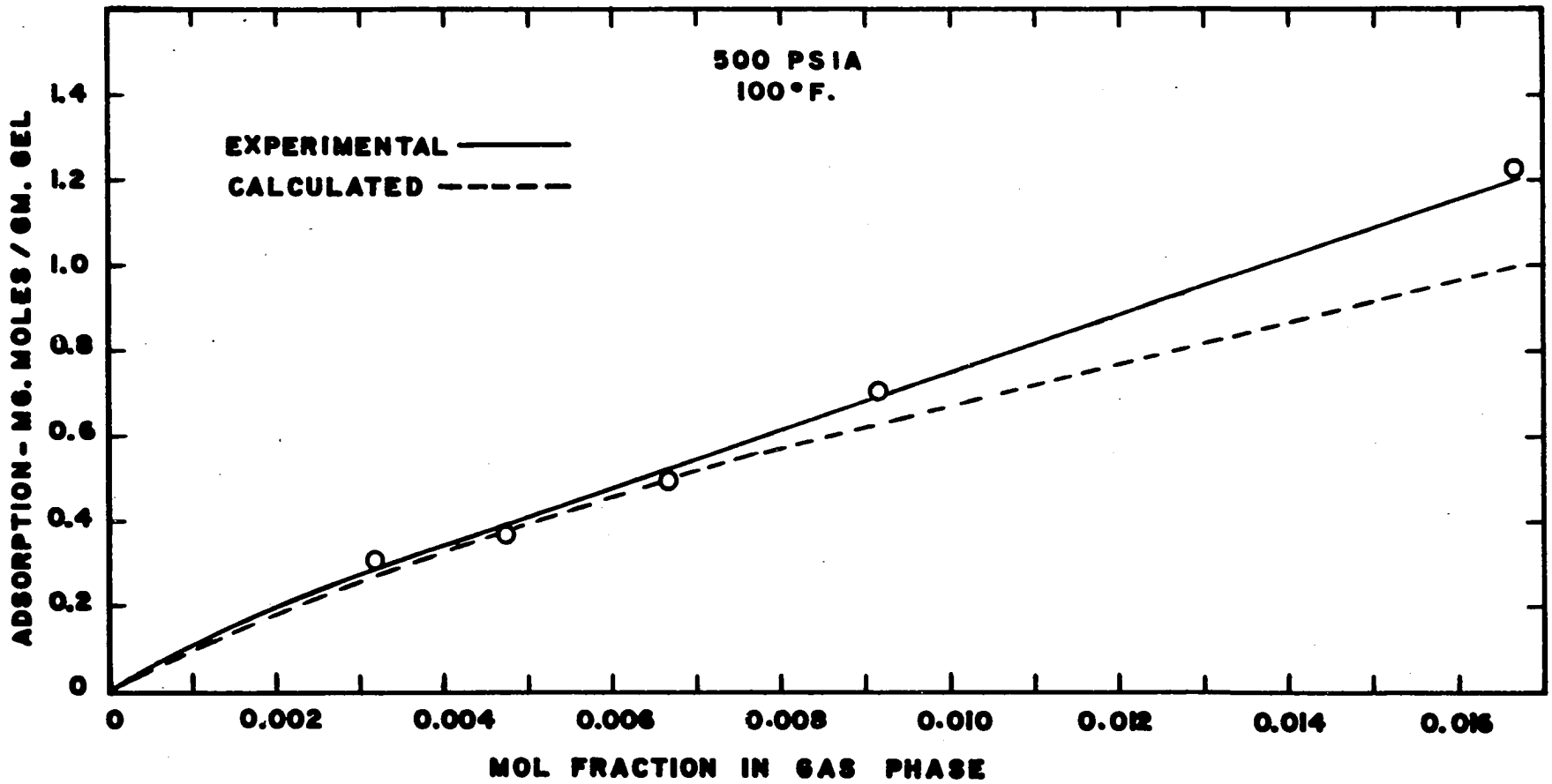

FIGURE 13 EFFECT OF CONCENTRATION ON nBUTANE ADSORPTION FROM METHANE - nBUTANE MIXTURES

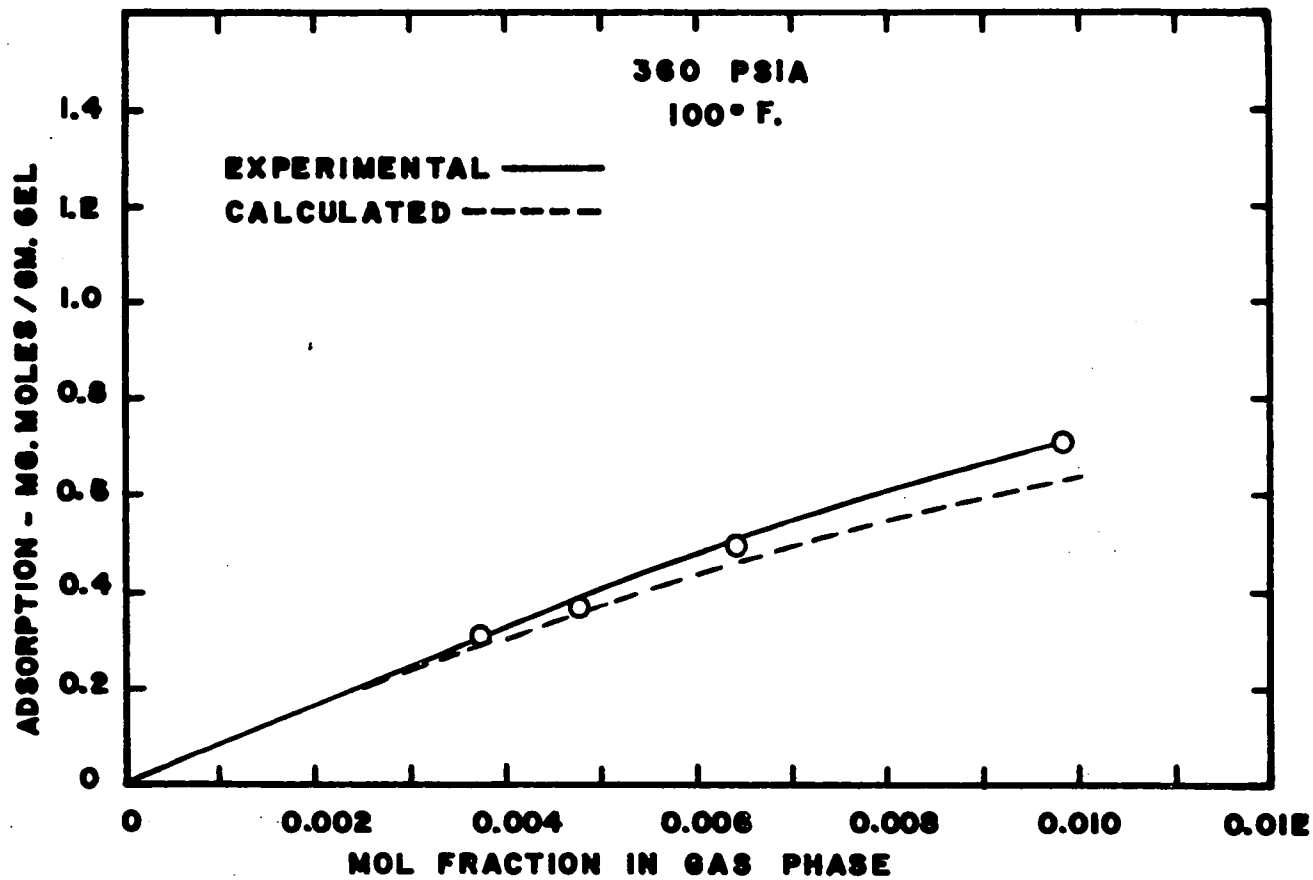

FIGURE 14 EFFECT OF CONCENTRATION ON nBUTANE ADSORPTION FROM METHANE - nBUTANE MIXTURES

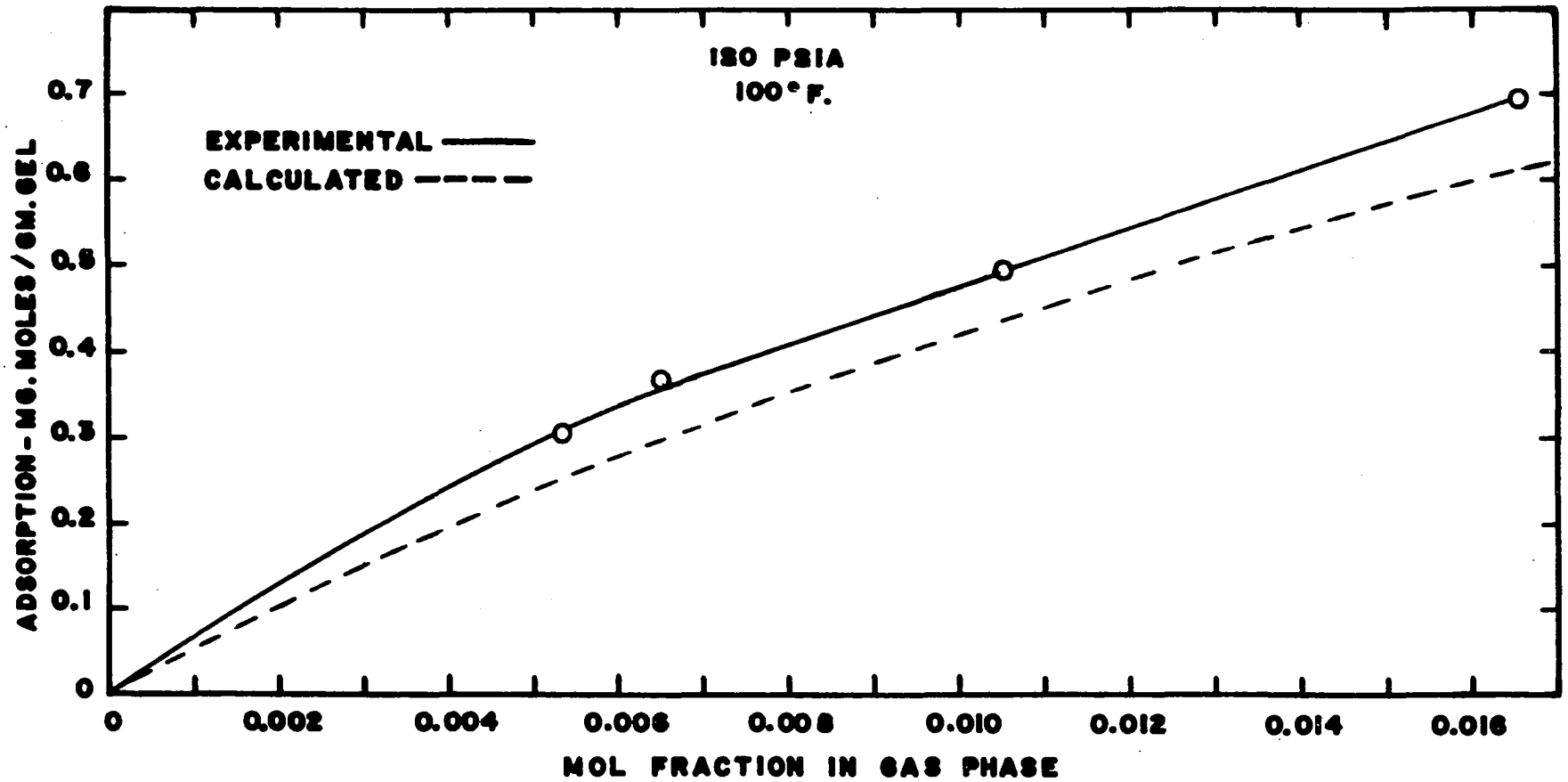

FIGURE 15 EFFECT OF CONCENTRATION ON nBUTANE ADSORPTION FROM METHANE - nBUTANE MIXTURES

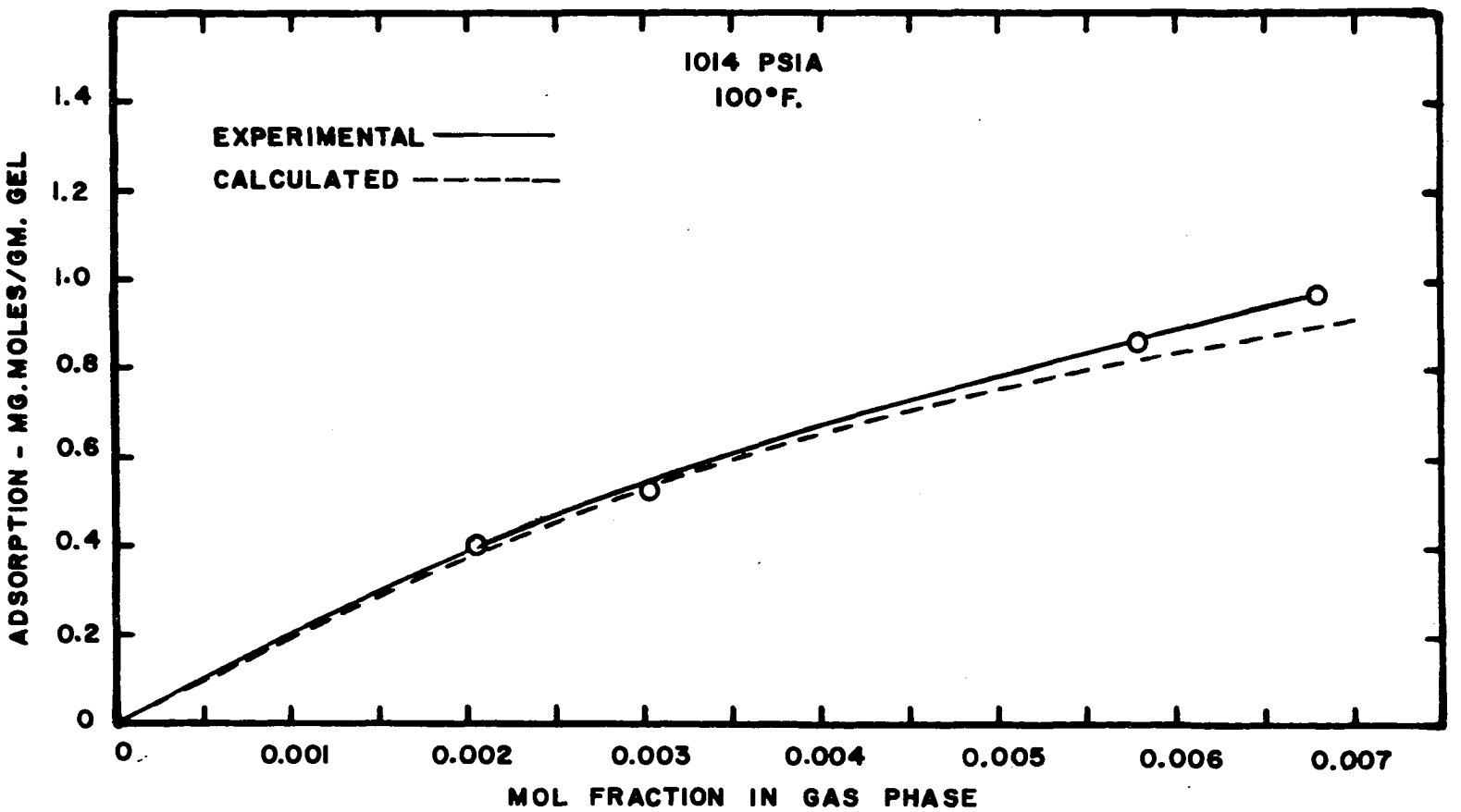

FIGURE 16 EFFECT OF CONCENTRATION ON nPENTANE ADSORPTION FROM METHANE-nPENTANE MIXTURES

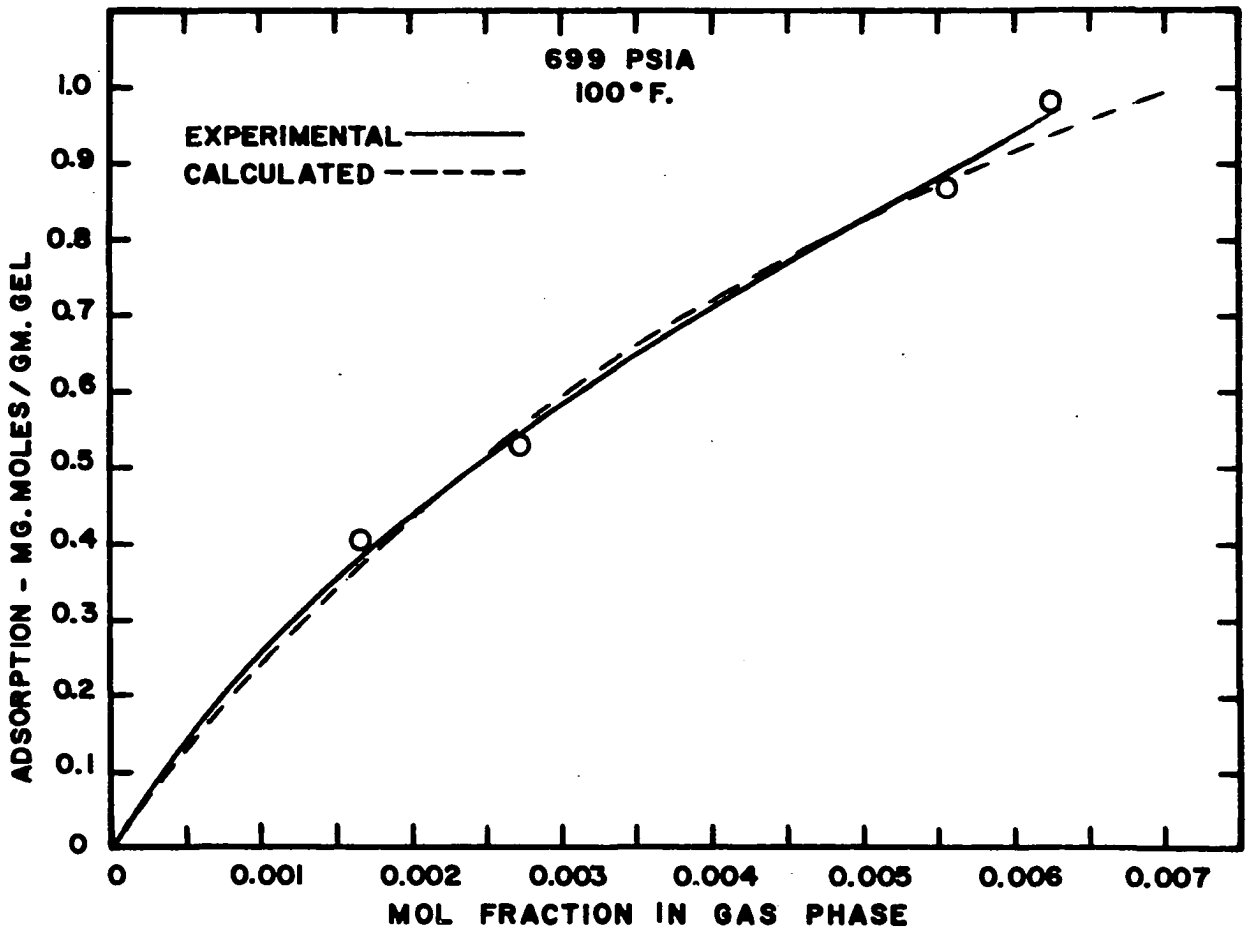

FIGURE 17 EFFECT OF CONCENTRATION ON nPENTANE ADSORPTION FROM METHANE - nPENTANE MIXTURES

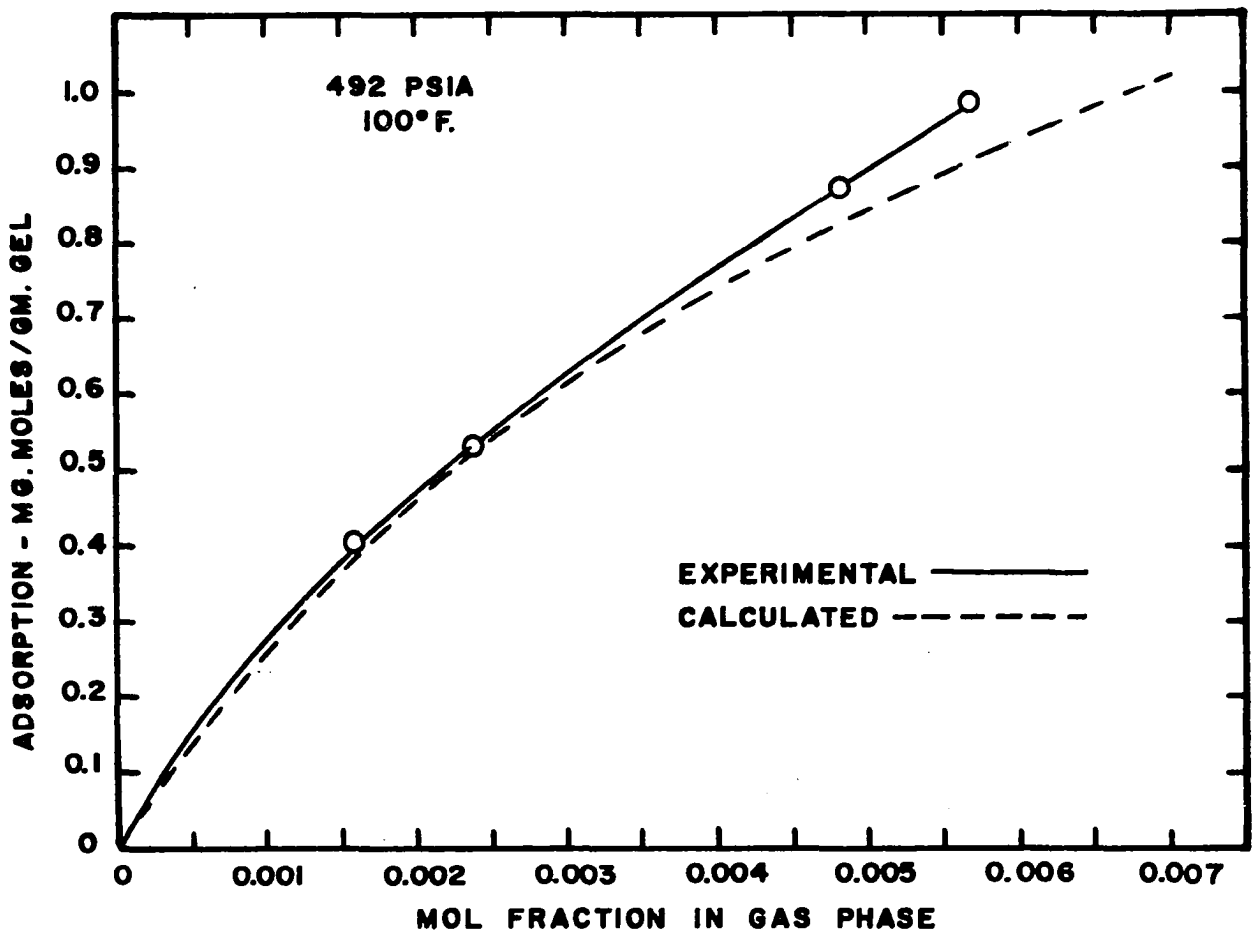

FIGURE 18 EFFECT OF CONCENTRATION ON nPENTANE ADSORPTION FROM METHANE - nPENTANE MIXTURES

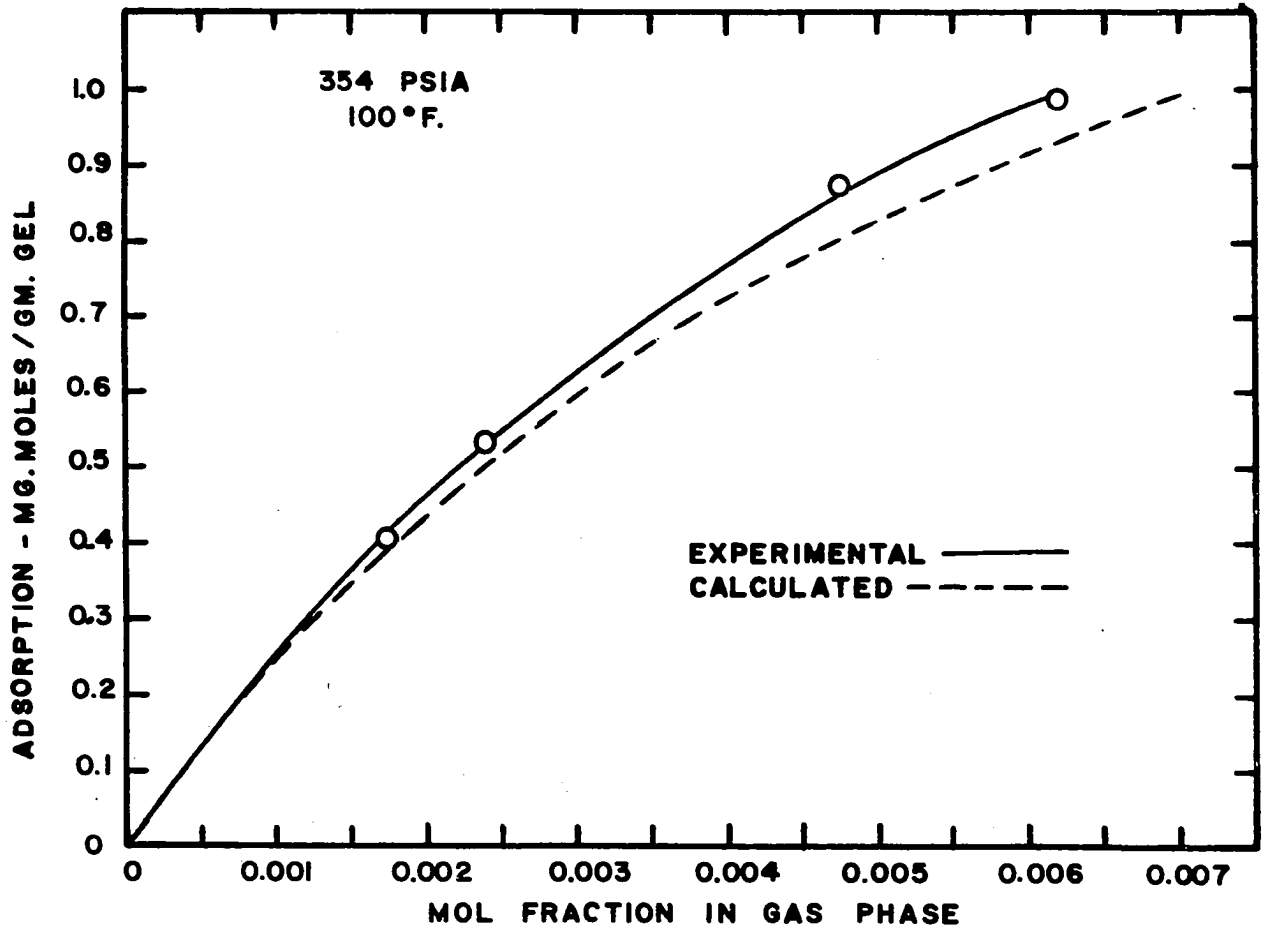

FIGURE 19 EFFECT OF CONCENTRATION ON nPENTANE ADSORPTION FROM METHANE - nPENTANE MIXTURES

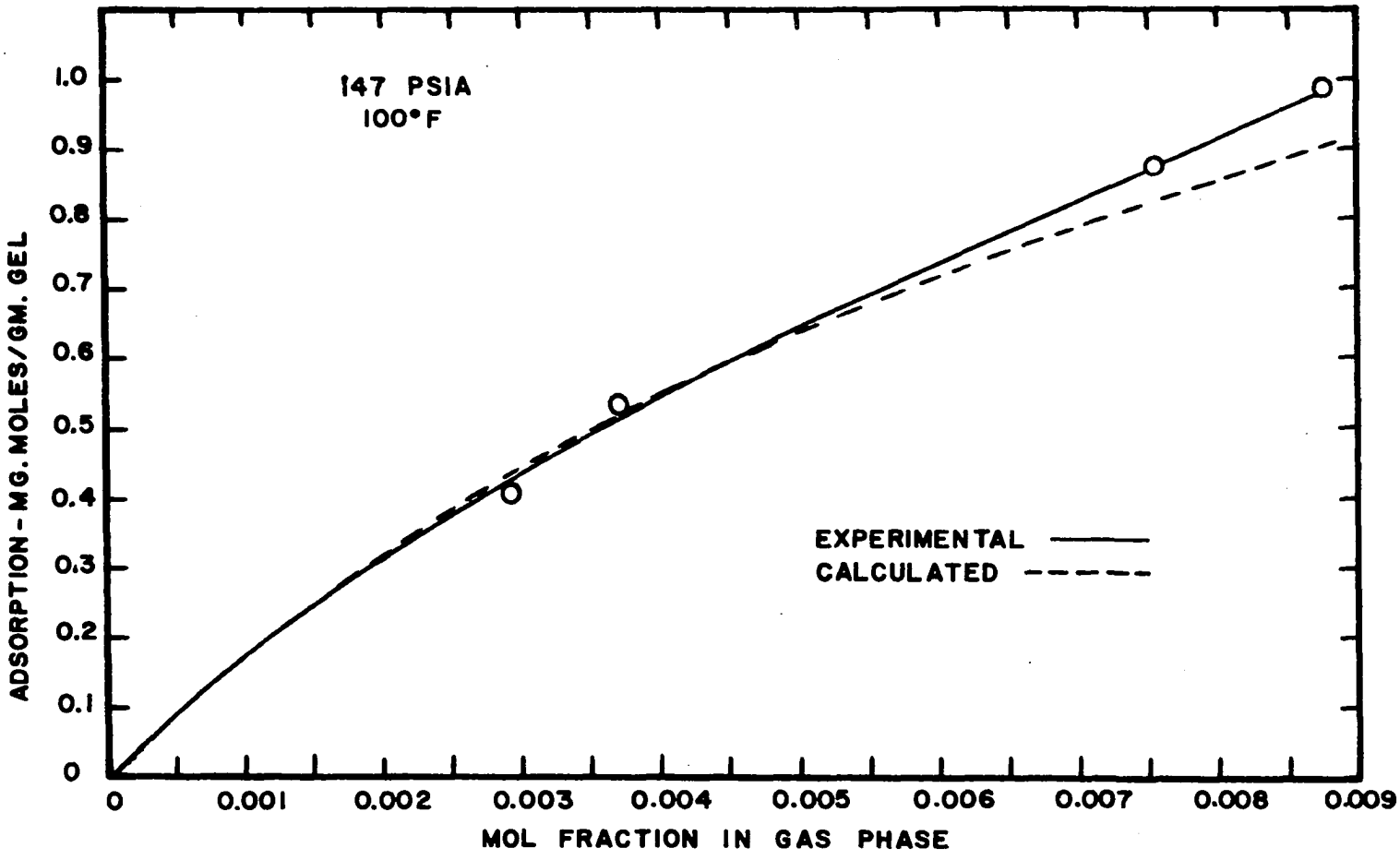

FIGURE 20 EFFECT OF CONCENTRATION ON nPENTANE ADSORPTION FROM METHANE - nPENTANE MIXTURES

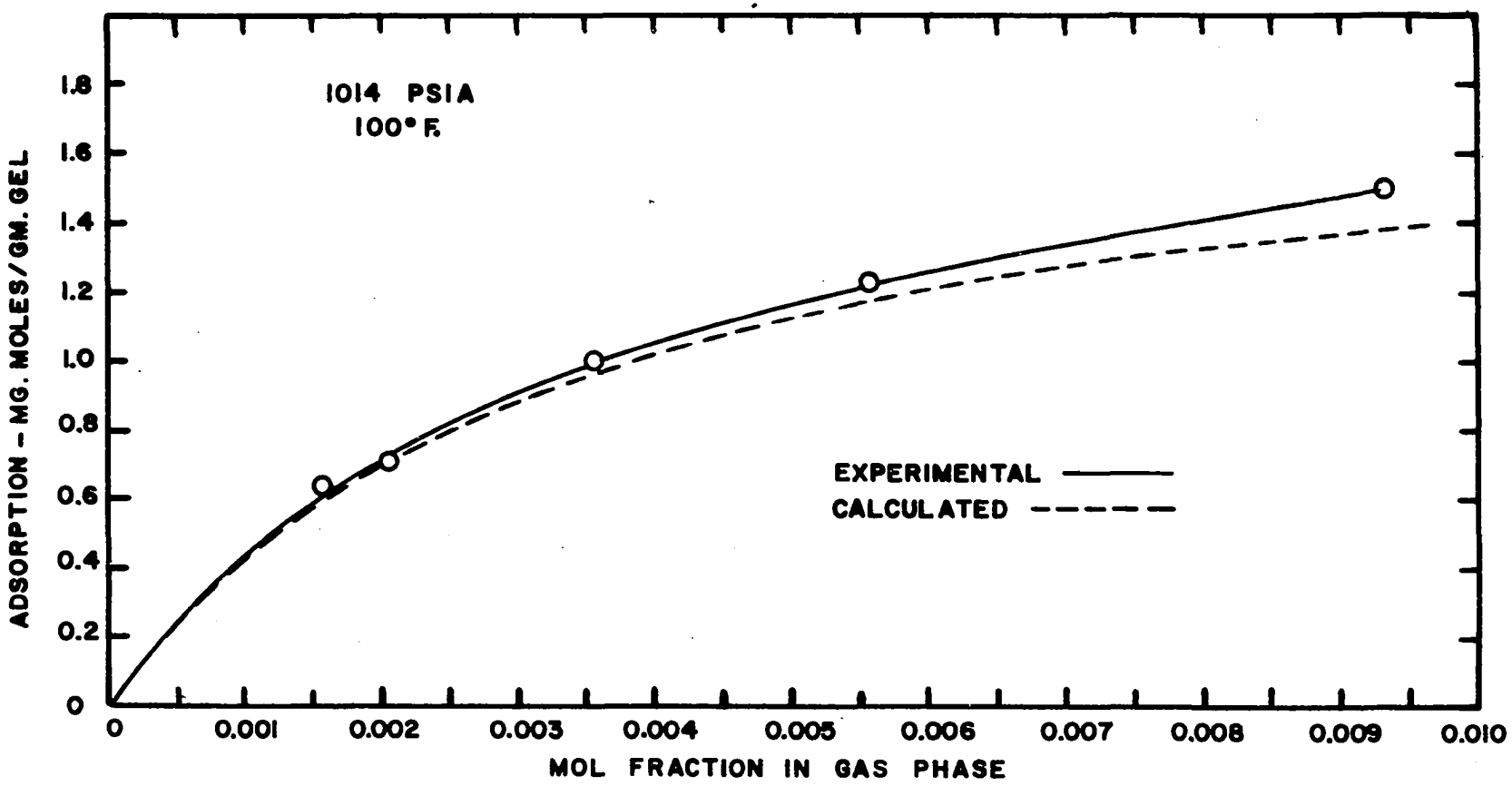

FIGURE 21 EFFECT OF CONCENTRATION ON nHEXANE ADSORPTION FROM METHANE - nHEXANE MIXTURES

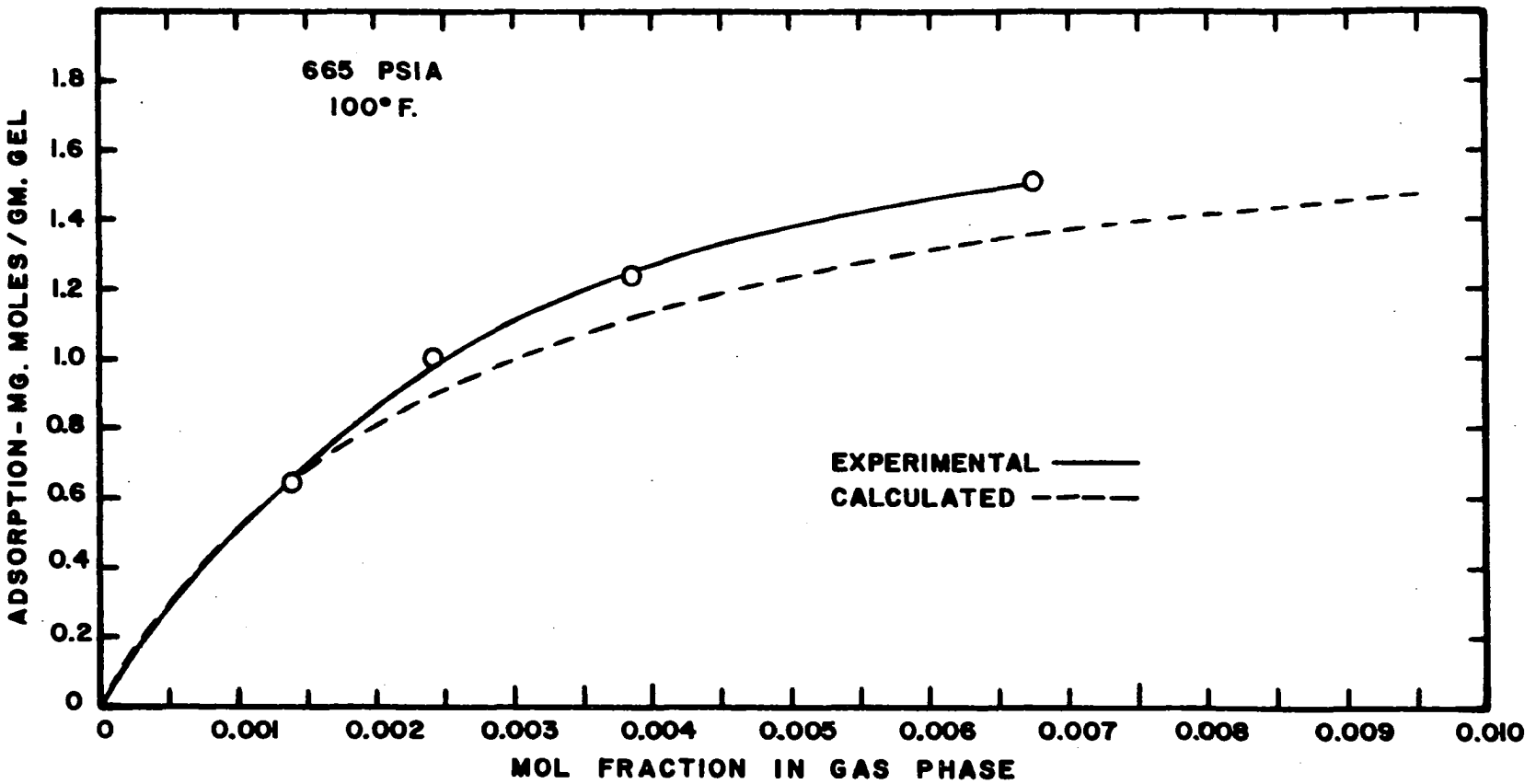

FIGURE 22 EFFECT OF CONCENTRATION ON nHEXANE ADSORPTION FROM METHANE - nHEXANE MIXTURES

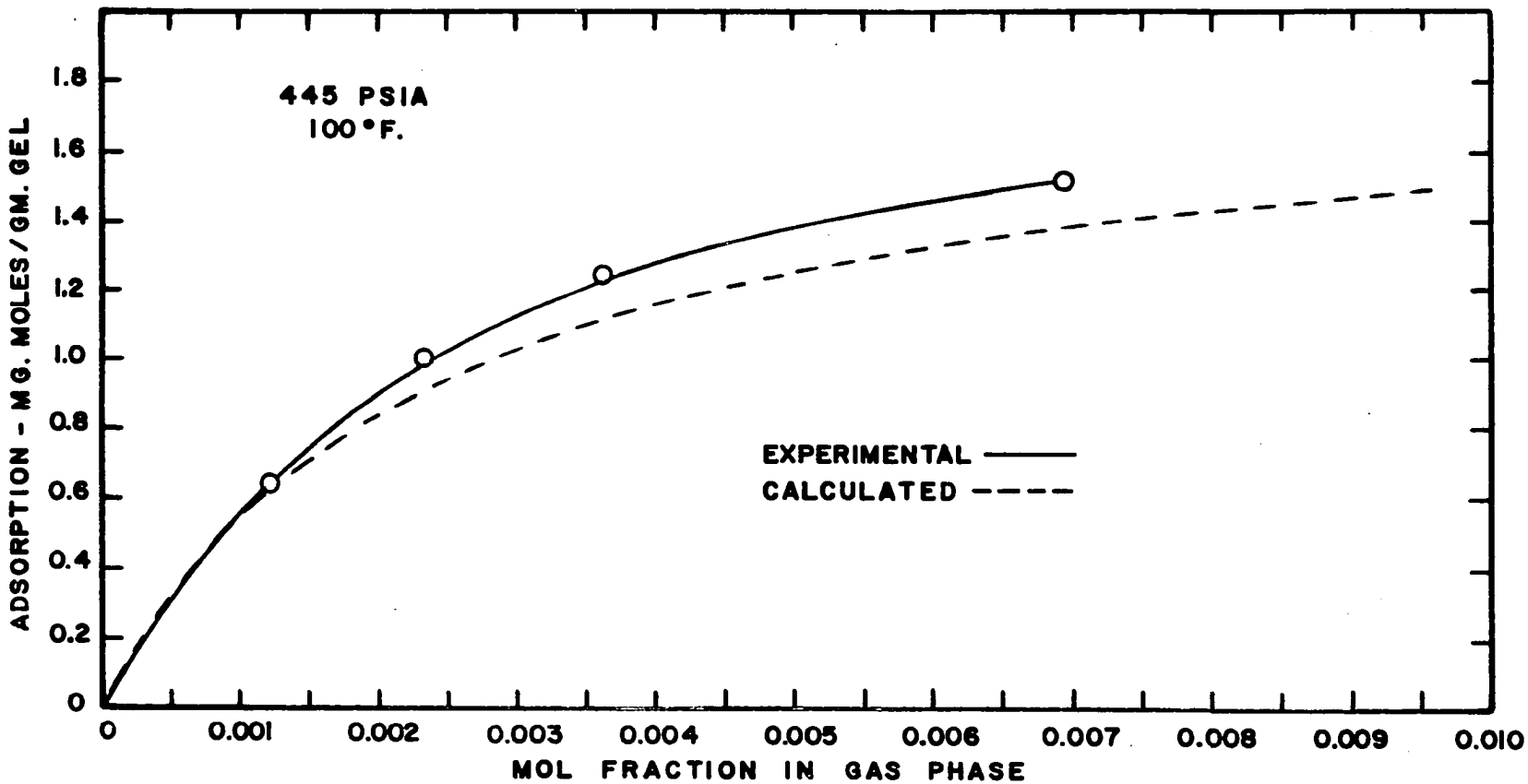

FIGURE 23 EFFECT OF CONCENTRATION ON nHEXANE ADSORPTION FROM METHANE - nHEXANE MIXTURES

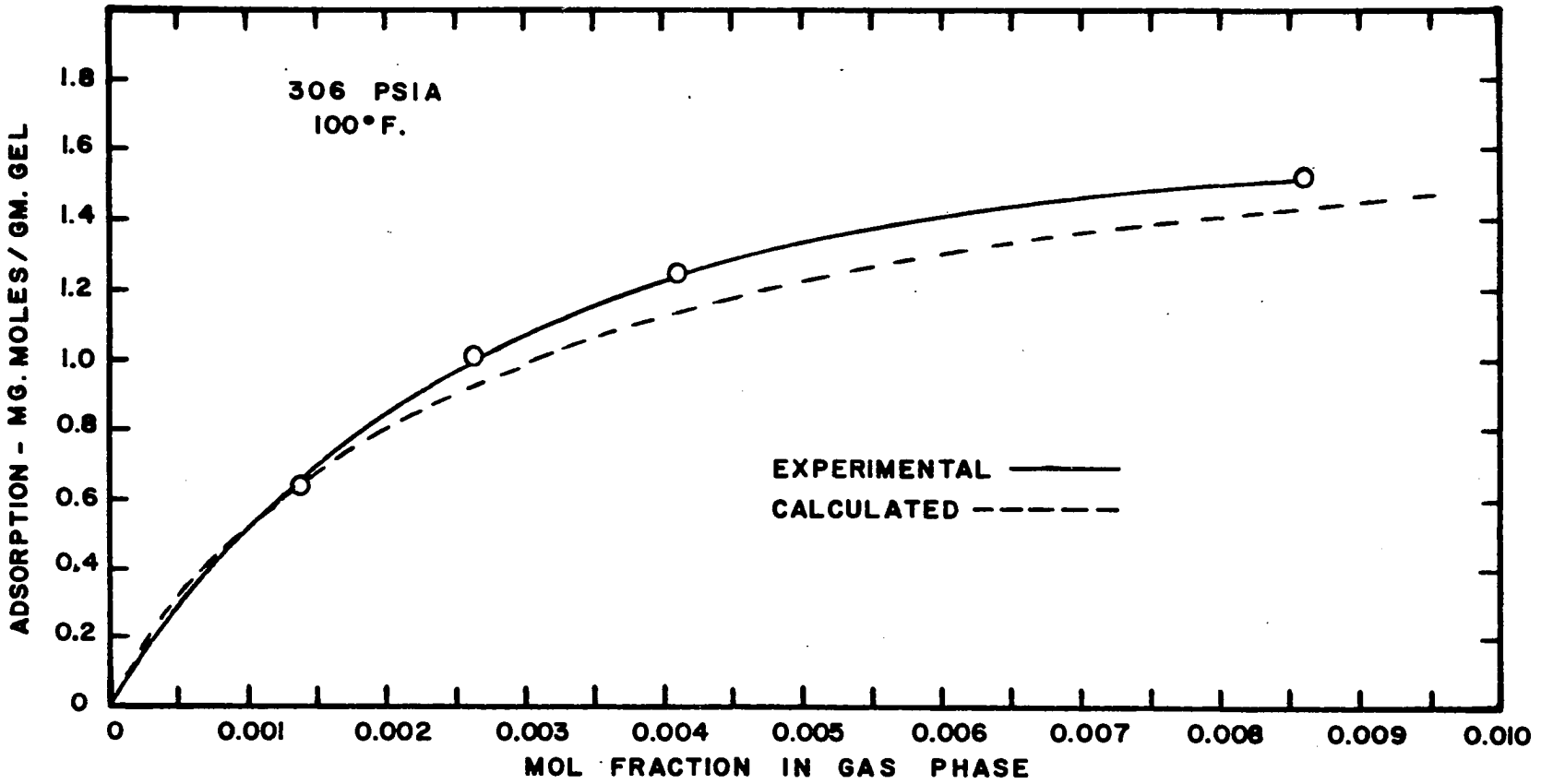

FIGURE 24 EFFECT OF CONCENTRATION ON nHEXANE ADSORPTION FROM METHANE - nHEXANE MIXTURES

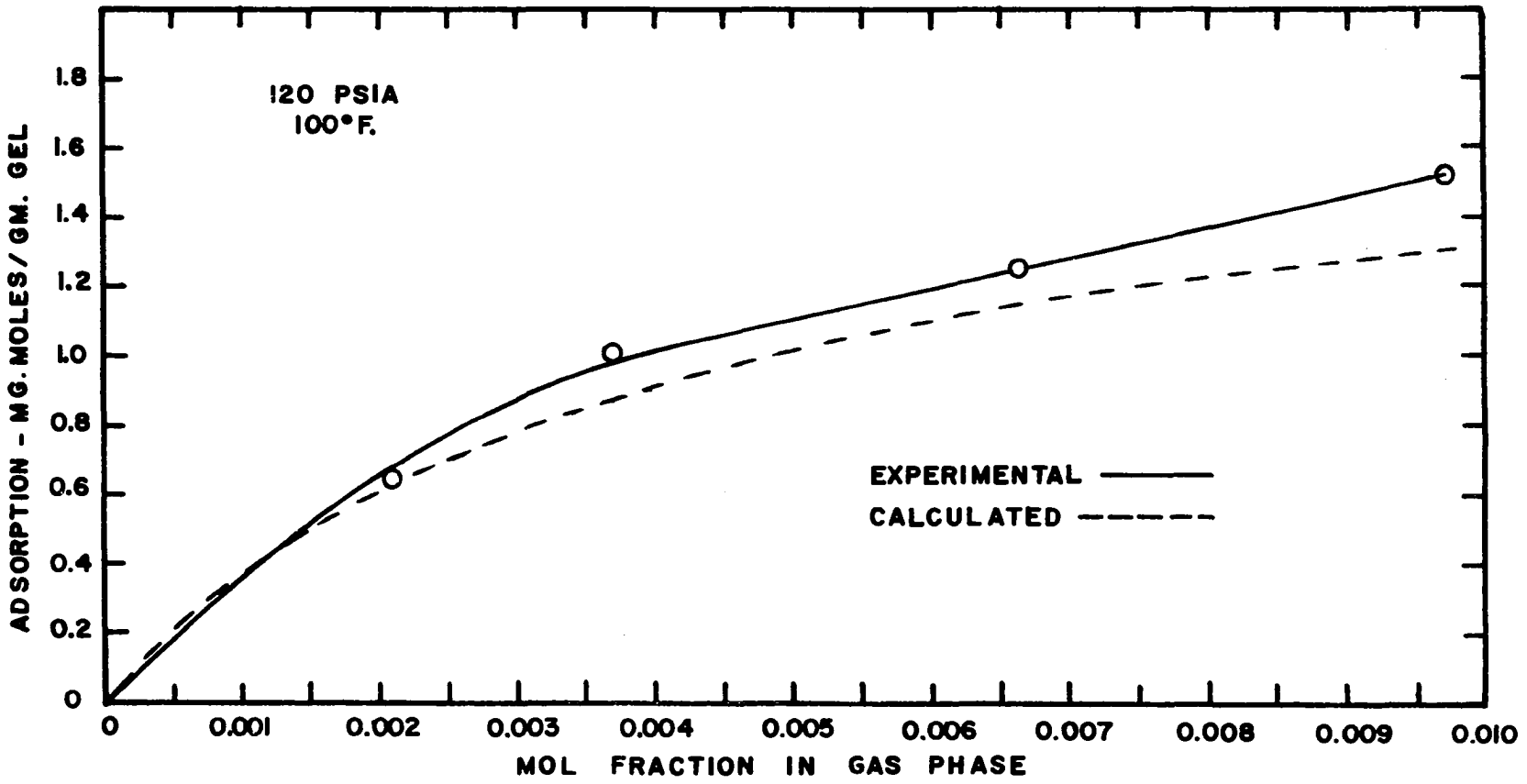

FIGURE 25 EFFECT OF CONCENTRATION ON nHEXANE ADSORPTION FROM METHANE - nHEXANE MIXTURES

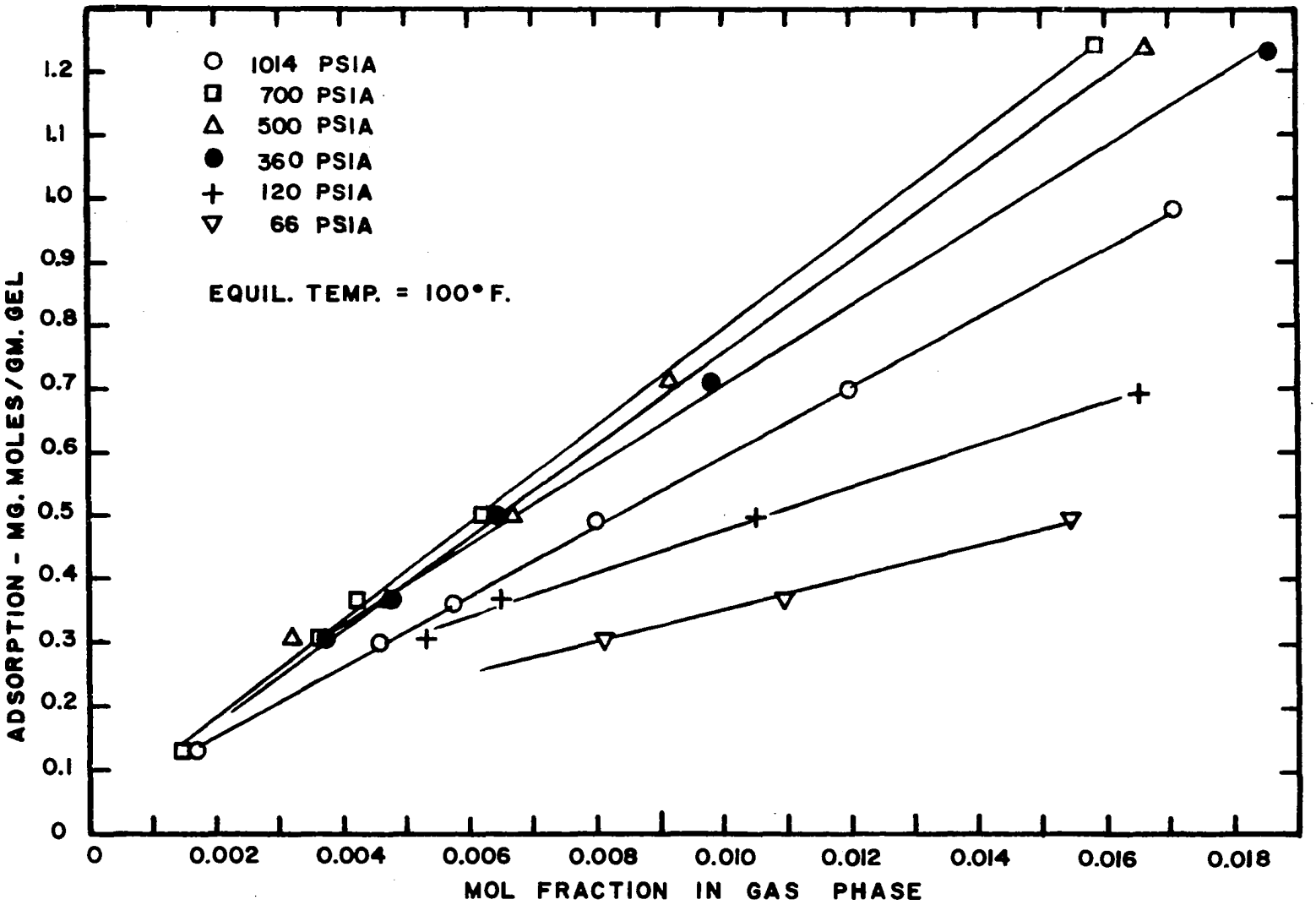

FIGURE 26 EFFECT OF CONCENTRATION AND PRESSURE ON nC_4 ADSORPTION FROM $C_1 - nC_4$ MIXTURES

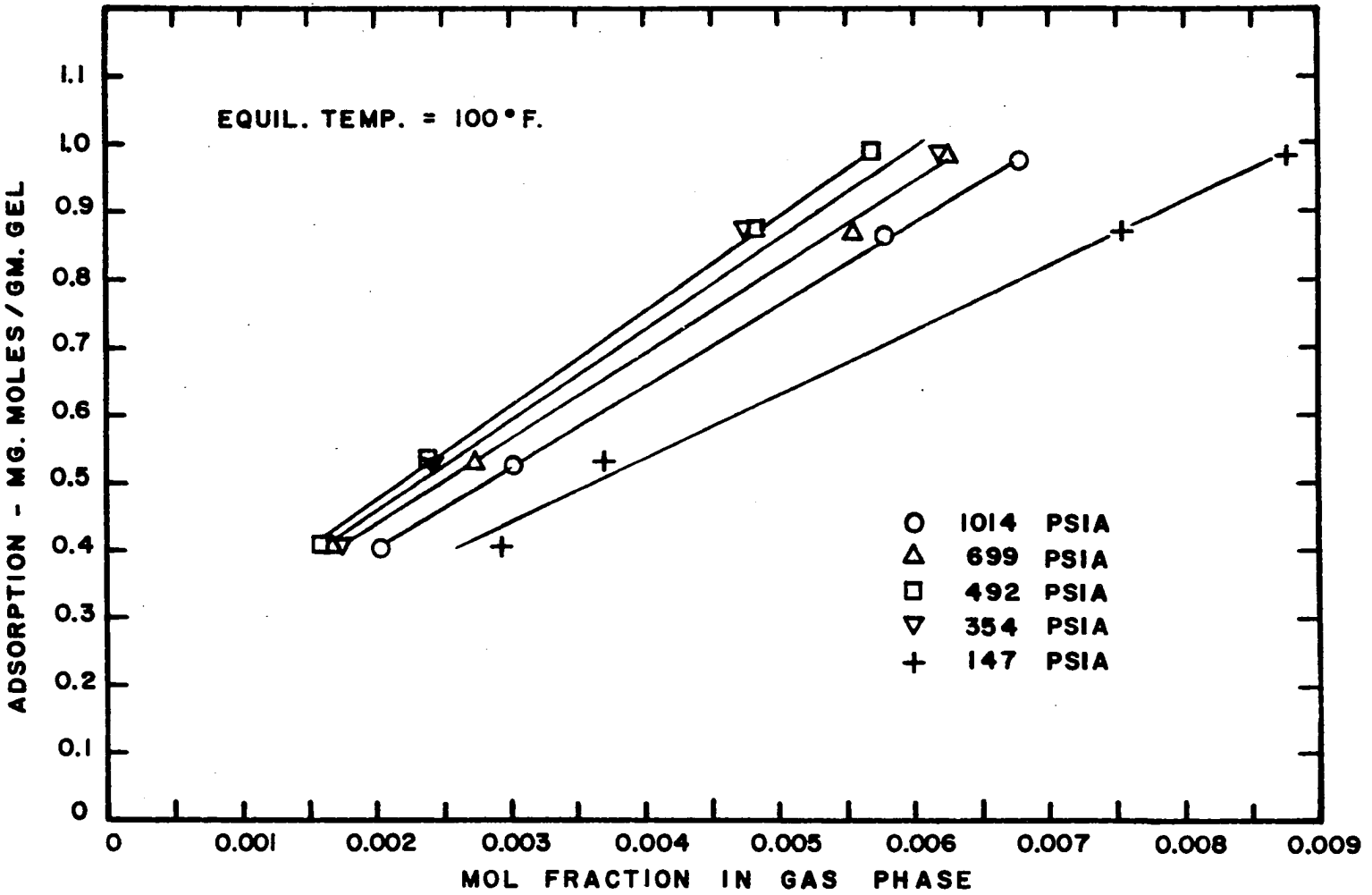

FIGURE 27 EFFECT OF CONCENTRATION AND PRESSURE ON nC_5 ADSORPTION FROM C_1 - nC_5 MIXTURES

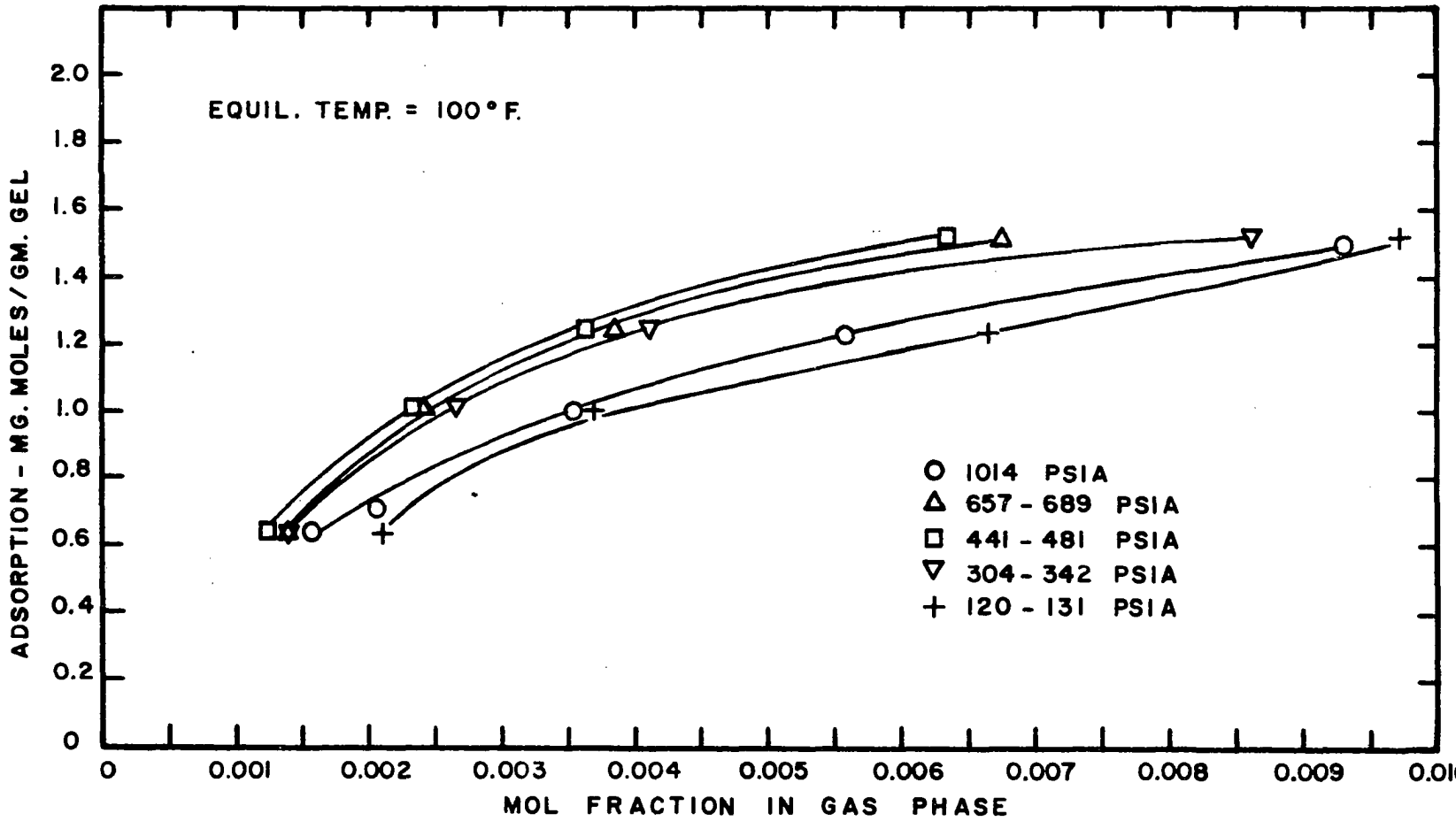

FIGURE 28 EFFECT OF CONCENTRATION AND PRESSURE ON nC_6 ADSORPTION FROM C_1 - nC_6 MIXTURES

$$v_{m4} = 2.39\ (800)/830 = 2.302 \text{ mg-moles/gm. gel.}$$

Referring again to Figure 5, and assuming a pore diameter of 21 angstrom units and a surface area of 800 square meters per gram, the v_{m4} so calculated on this idealized basis is as follows:

$$\text{Total surface area} = 800\ (19.64 \text{ grams}) = 15{,}712 \text{ m.}^2$$

The length of a capillary of 21 angstrom units diameter having an internal surface area of 15,712 m.^{2} is:

$$\pi DL = 15{,}712 \text{ m}^2$$

or,
$$L = (15{,}712 \times 10^3)/(\pi \times 21 \times 10^{-10} \text{ meters})$$

$$= 0.238 \times 10^{13} \text{ meters.}$$

The length of an n-butane molecule was reported by Hirschfelder (9) to be 8.72 angstrom units = 8.72×10^{-8} centimeters. Thus, the number of molecules adsorbed on the capillary tube walls in one monolayer is:

$$(10 \text{ rows})\ (0.238 \times 10^{13})/(8.72 \times 10^{-10}) =$$

$$= 0.2728 \times 10^{23} \text{ molecules.}$$

The number of gram-moles of n-butane adsorbed is:

$$(0.2728 \times 10^{23})/(6.024 \times 10^{23}) = 0.0453 \text{ gram-moles,}$$

or, in other units of adsorption,

$$v_m = 0.0453\ (1000)/19.64 \text{ grams} =$$

$$= 2.304 \text{ mg-moles/gm gel.}$$

This value of v_m (monolayer coverage) is identical with that determined in the Mason and Cooke work for pure component n-butane.

The adsorbed area per molecule may be determined as

$$(15{,}712\ m^2)(10^{+20}\ \mathring{A}^2/m^2)/(0.2728 \times 10^{23} \text{ molecules}) =$$

$$= 57.6\ \mathring{A}^2 \text{ adsorbed area/molecule.}$$

This value of 57.6 $\mathring{A}^2$ for an adsorbed n-butane molecule is, likewise, identical with that reported by Mason and Cooke from their BET plots of pure component data. Thus, it is concluded that the arguments for monolayer adsorption discussed previously are reasonable and sound. It is further concluded that the constants in Table 1 may be used in further calculations in present or future work.

Experimental and Calculated Results - Ternary Runs

Inasmuch as any useful correlation for binary mixtures must also satisfactorily predict the adsorption of ternary mixtures, three systems of methane, n-pentane, and n-hexane were run to show the effects of additional components upon the adsorption and to provide a means of checking the prediction technique outlined in Appendix A. These results are summarized in Table 2. Inspection of the table shows further remarkably good agreement between the experimental and predicted values at all pressure levels. Thus, the validity and applicability of the theoretical monolayer model of adsorption is

concluded to be well satisfied and so established. Such correlations should be extremely useful in future commercial applications in the design and evaluation of hydrocarbon adsorption units in the petroleum industry.

Effect of Additional Components

The effect of additional components in Table 2 is quite pronounced. The effect is to decrease the adsorption of a given component by the addition of another component to the mixture, increasing the competition between the components for occupancy of available surface sites. This effect was thought due to the competition between components for the surface sites, as well as a reduction in the pentane fugacity with the addition of other components to the mixture.

Effect of Concentration

The effect of concentration of a given component in the equilibrium gas phase can be seen in Figure 10 for n-butane, n-pentane, and n-hexane. These results show increasing adsorption with increasing concentration of the heavier component in the binary mixtures. Adsorption also increases with increasing molecular weight.

Effect of Total Pressure

Figures 26-31 show the effects of total system pressure upon the adsorption from binary mixtures at given concentration levels. Experimental values are compared with the predicted values in Figures 29-31 and show excellent agreement again. The curves show the adsorption passing through a maximum and declining at the higher pressures. This

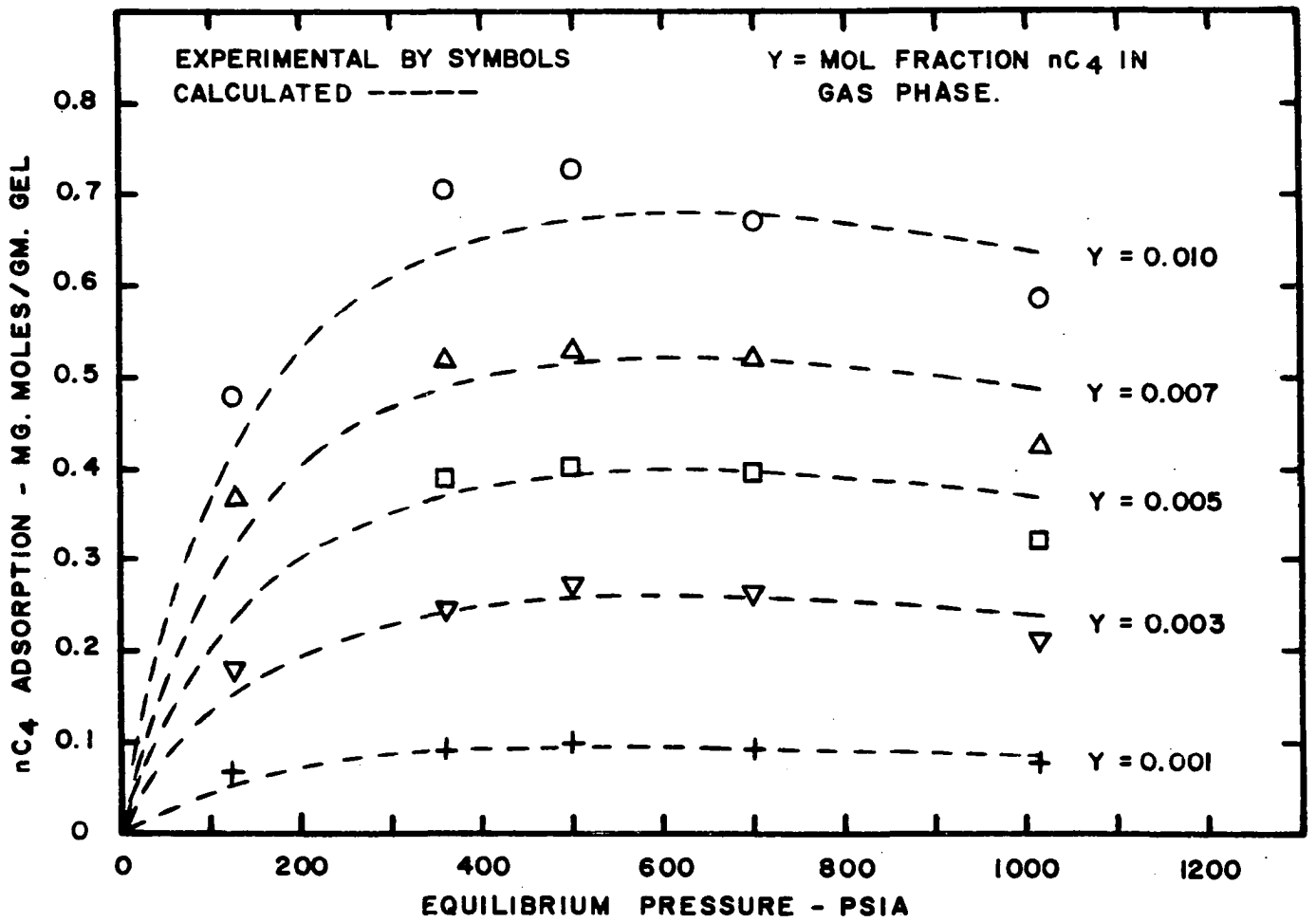

FIGURE 29 EFFECT OF PRESSURE ON nBUTANE ADSORPTION FROM METHANE - nBUTANE MIXTURES, 100° F.

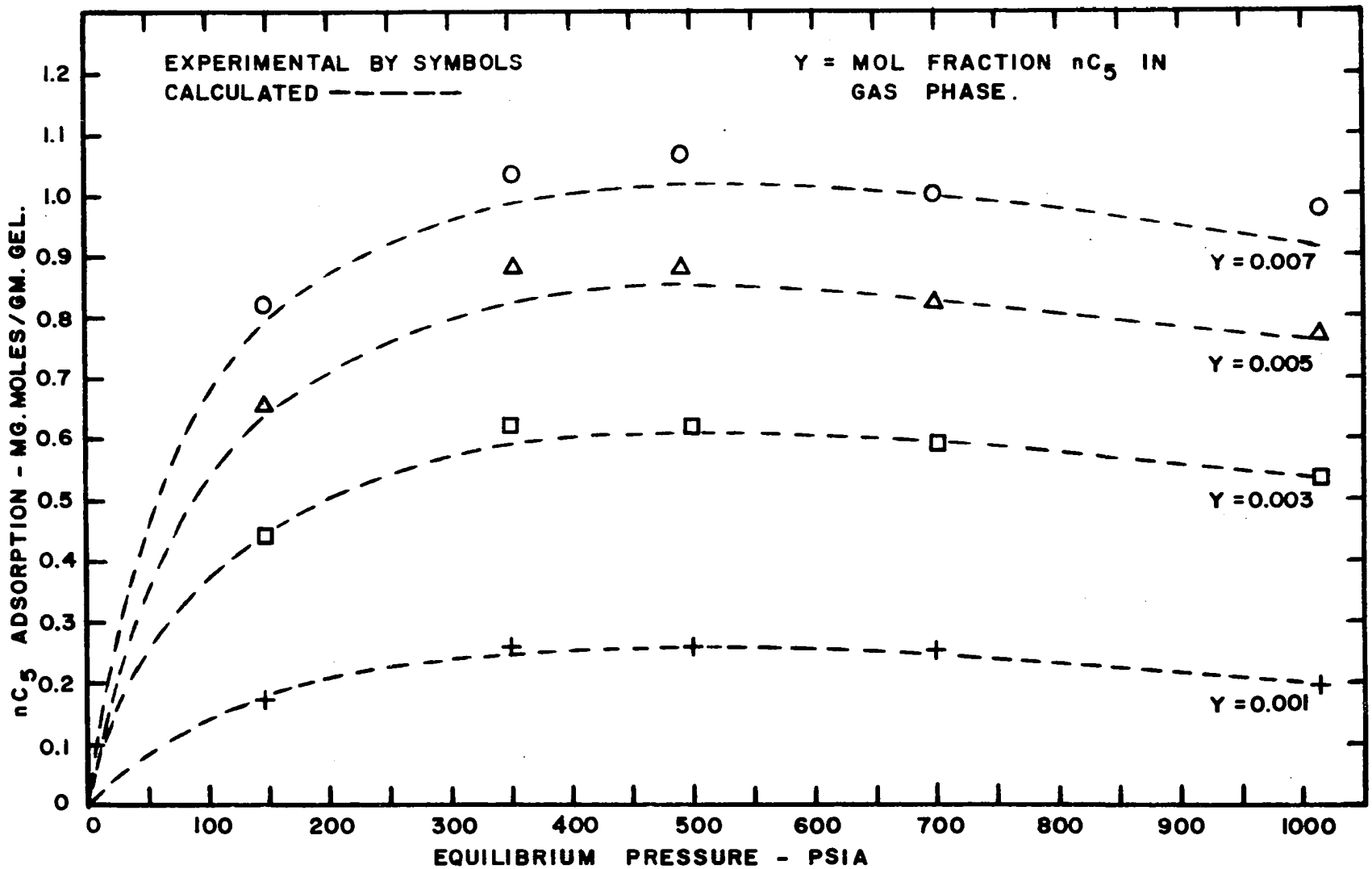

FIGURE 30 EFFECT OF PRESSURE ON nPENTANE ADSORPTION FROM METHANE - nPENTANE MIXTURES

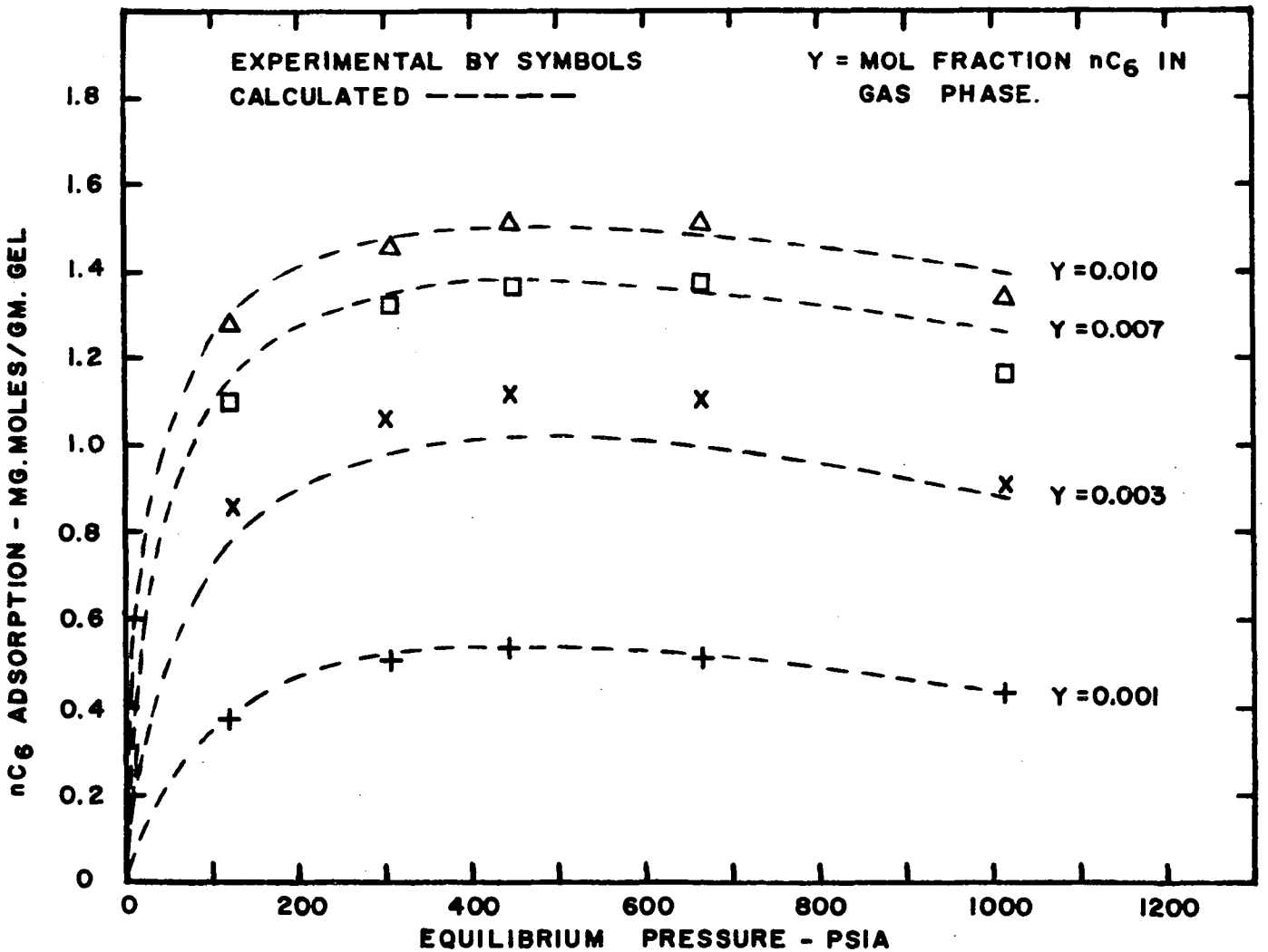

FIGURE 31 EFFECT OF PRESSURE ON nHEXANE ADSORPTION FROM METHANE - nHEXANE MIXTURES

effect may be explained on the basis of decreasing fugacities of the heavier components at the higher pressures, while the methane fugacity does not behave in such a manner. Thus, it is suggested that methane molecules become increasingly competitive for available surface sites.

In general, in all of the mixtures investigated the gas that was preferentially adsorbed was that pure gas for which the pure adsorbent capacity was the greatest. Mutual competition and interference between the gases in the mixture caused a lower adsorption for a given component than was observed in reported pure component data.

Empirical Correlations

Since the experimental results showed such good agreement with the theoretical isotherm, and since the technique rather simply describes the physical model of adsorption, further empirical correlations would seem to be redundant and less meaningful. However, three such empirical correlations are shown in Figures 32-35. Figure 33 shows a linear relationship between the reciprocal of amount adsorbed and square root of the vapor-adsorbate equilibrium ratio. Values for calculating K were obtained from Figure 32, a plot of mol fraction of n-butane in the adsorbed phase versus its mol fraction in the equilibrium gas phase. The values so determined for Figure 33 are tabulated in Table 16. Such correlations are limited to the pressure for which it was developed, in this case for 1014 psia, and other such correlations would have to be developed for other pressure levels. Figure 34 shows such a linear relationship for all three hydrocarbons, n-butane, n-pentane, and n-hexane.

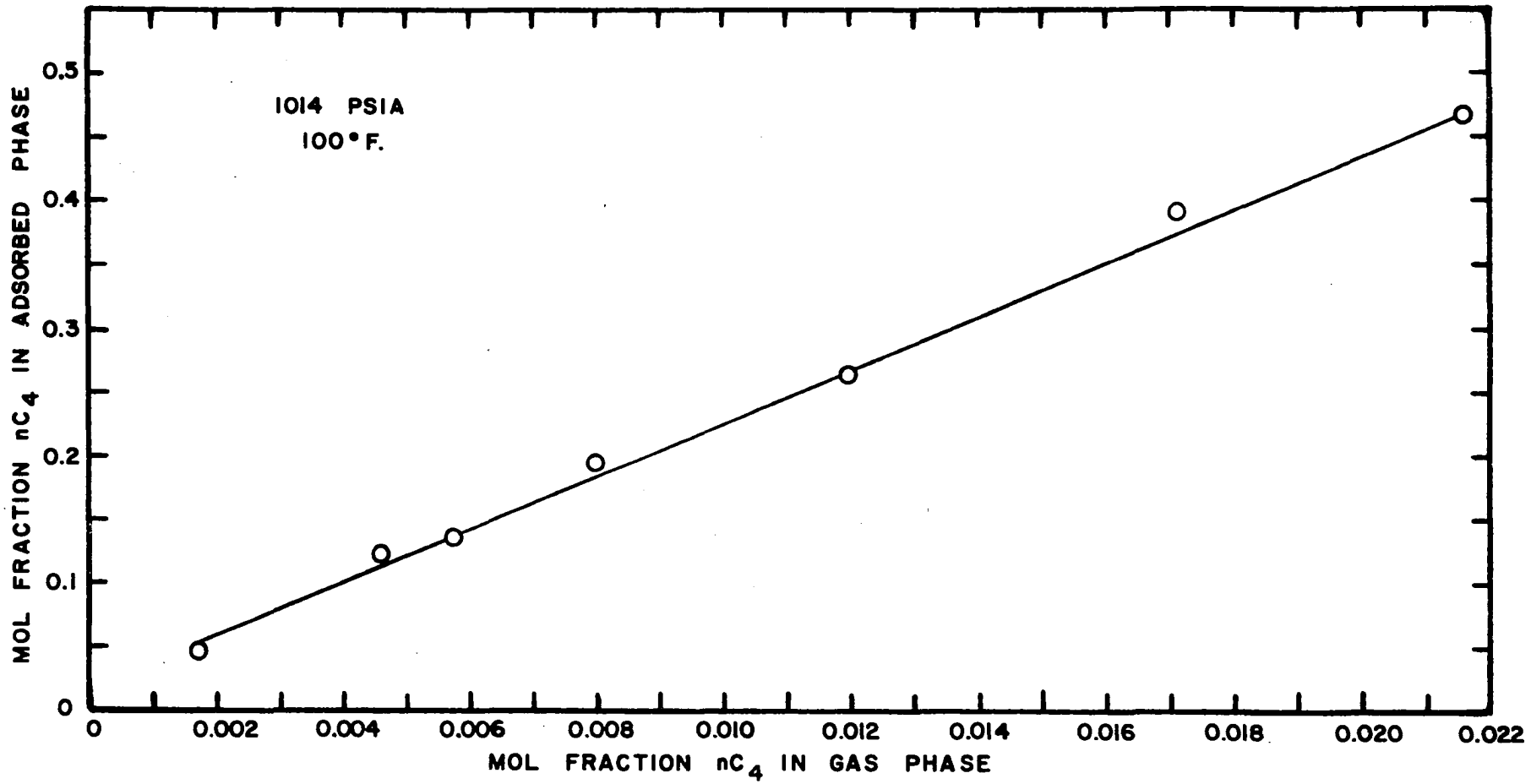

FIGURE 32 MOL FRACTION nC_4 IN ADSORBED PHASE VERSUS MOL FRACTION nC_4 IN GAS PHASE

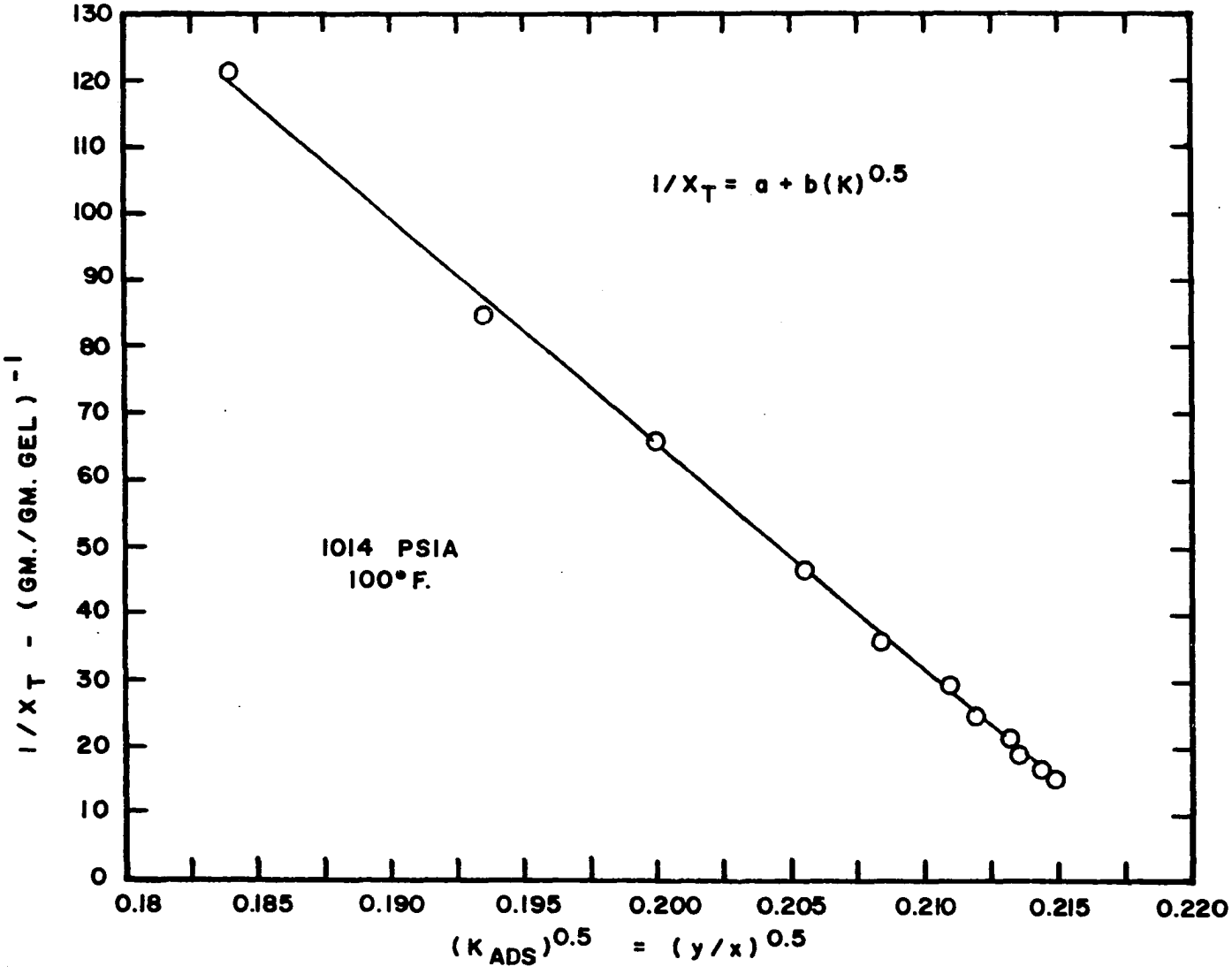

FIGURE 33 CORRELATION OF nC_4 ADSORPTION WITH EQUILIBRIUM RATIO

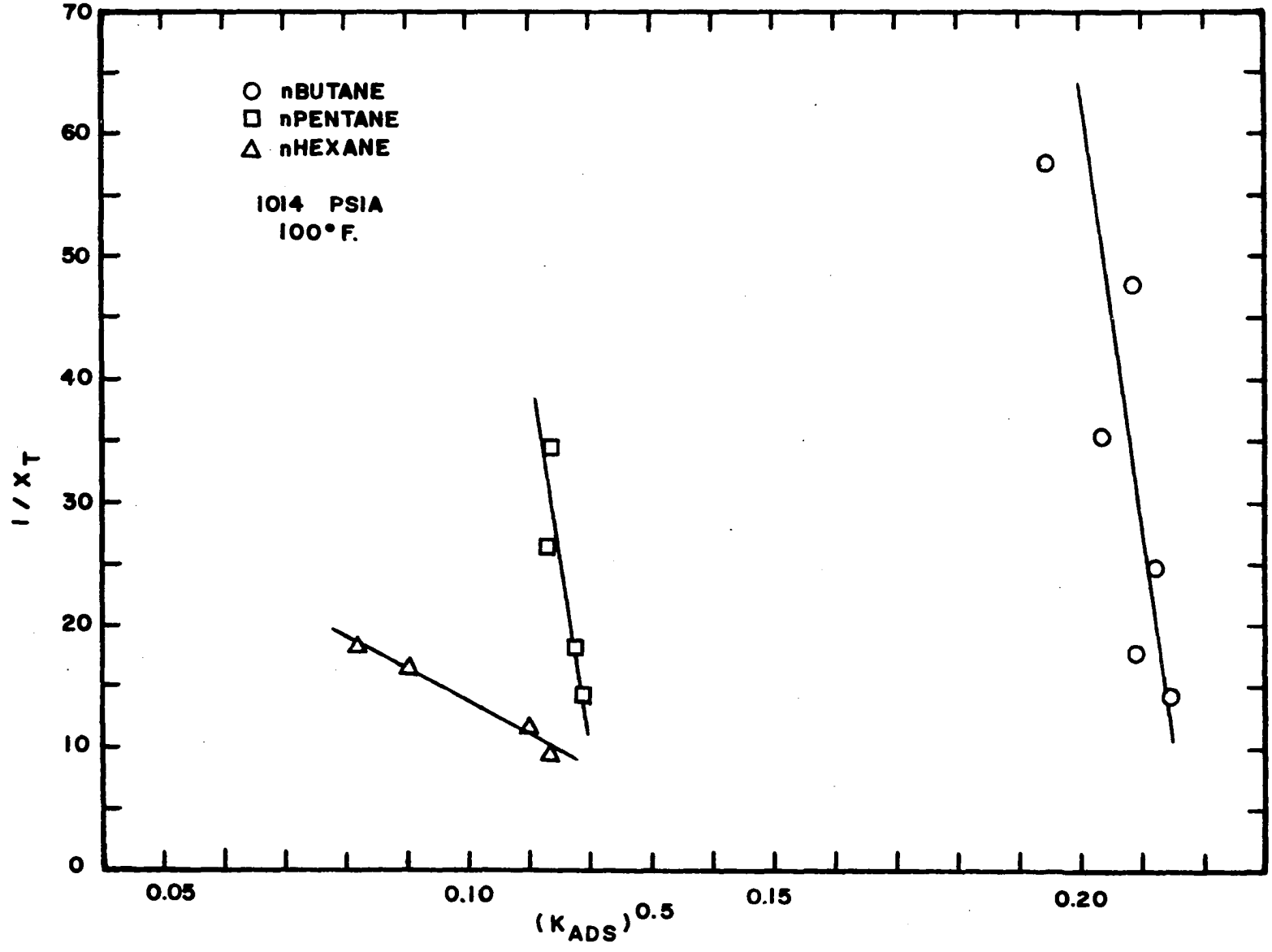

FIGURE 34 CORRELATION OF nC_4, nC_5, nC_6 ADSORPTION WITH EQUILIBRIUM RATIO

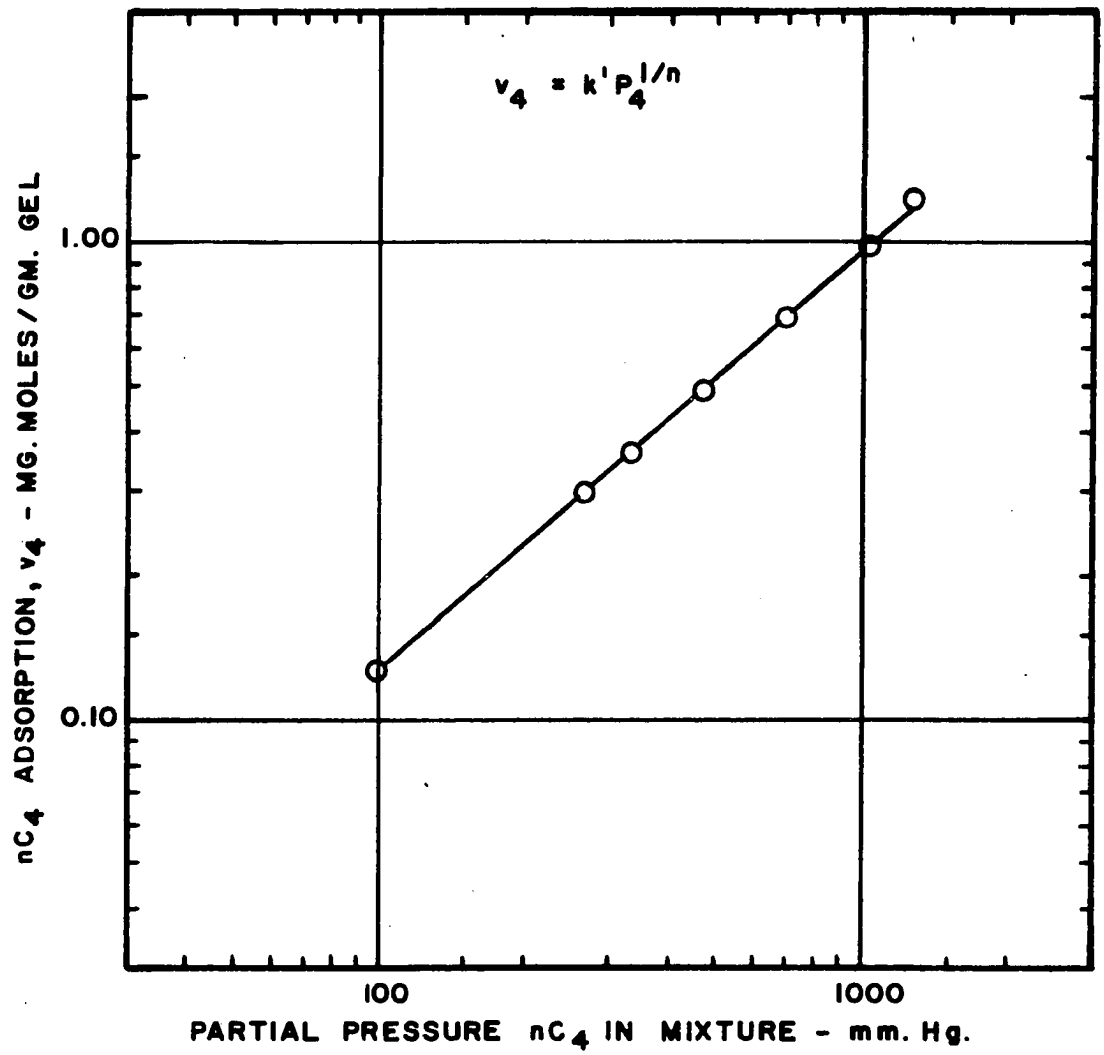

FIGURE 35 FREUNDLICH-TYPE ISOTHERMS
1014 PSIA, 100°F.

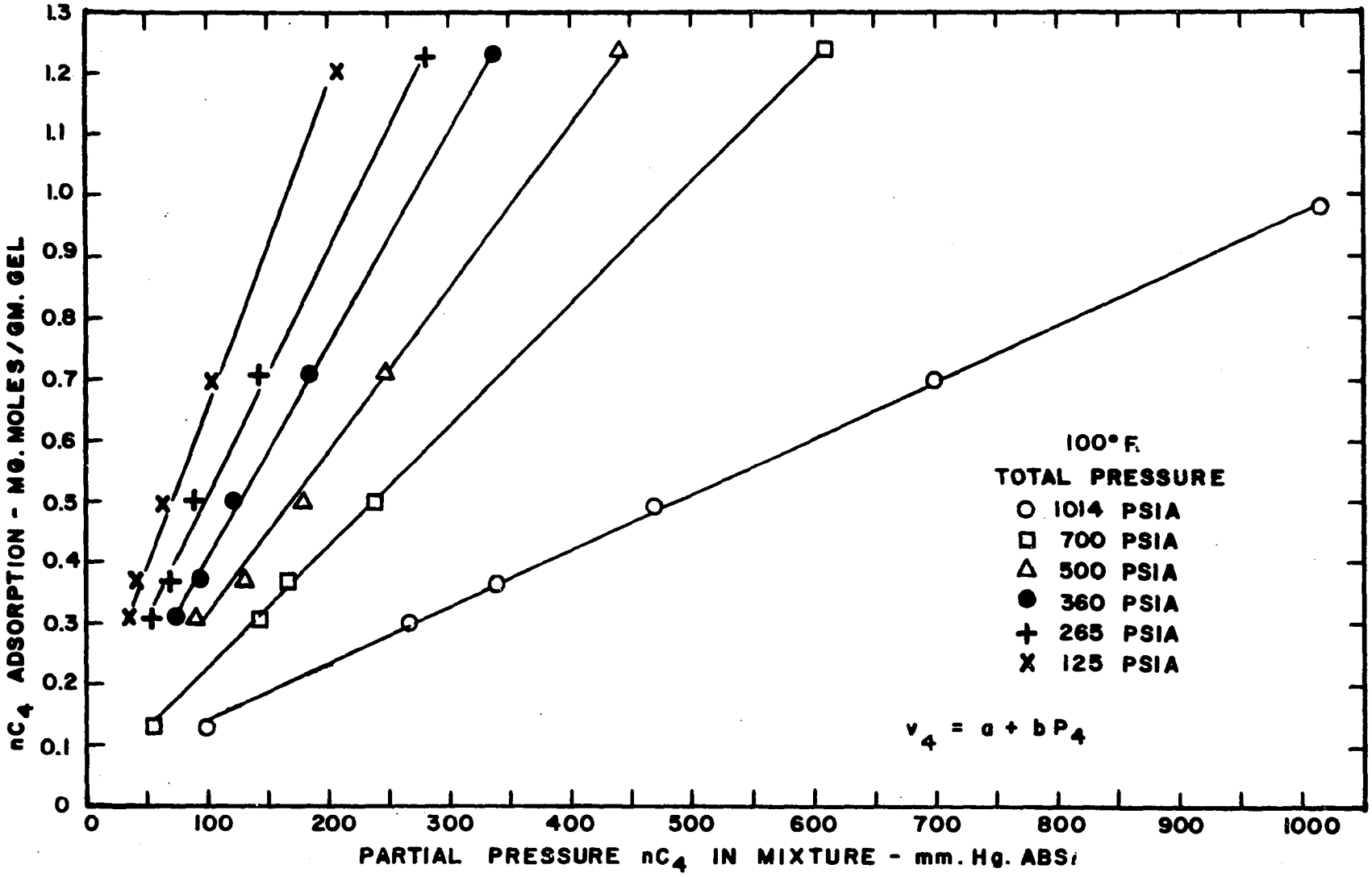

FIGURE 36 EFFECT OF PARTIAL PRESSURE OF nC_4 ON ADSORPTION FROM C_1 - nC_4 MIXTURES

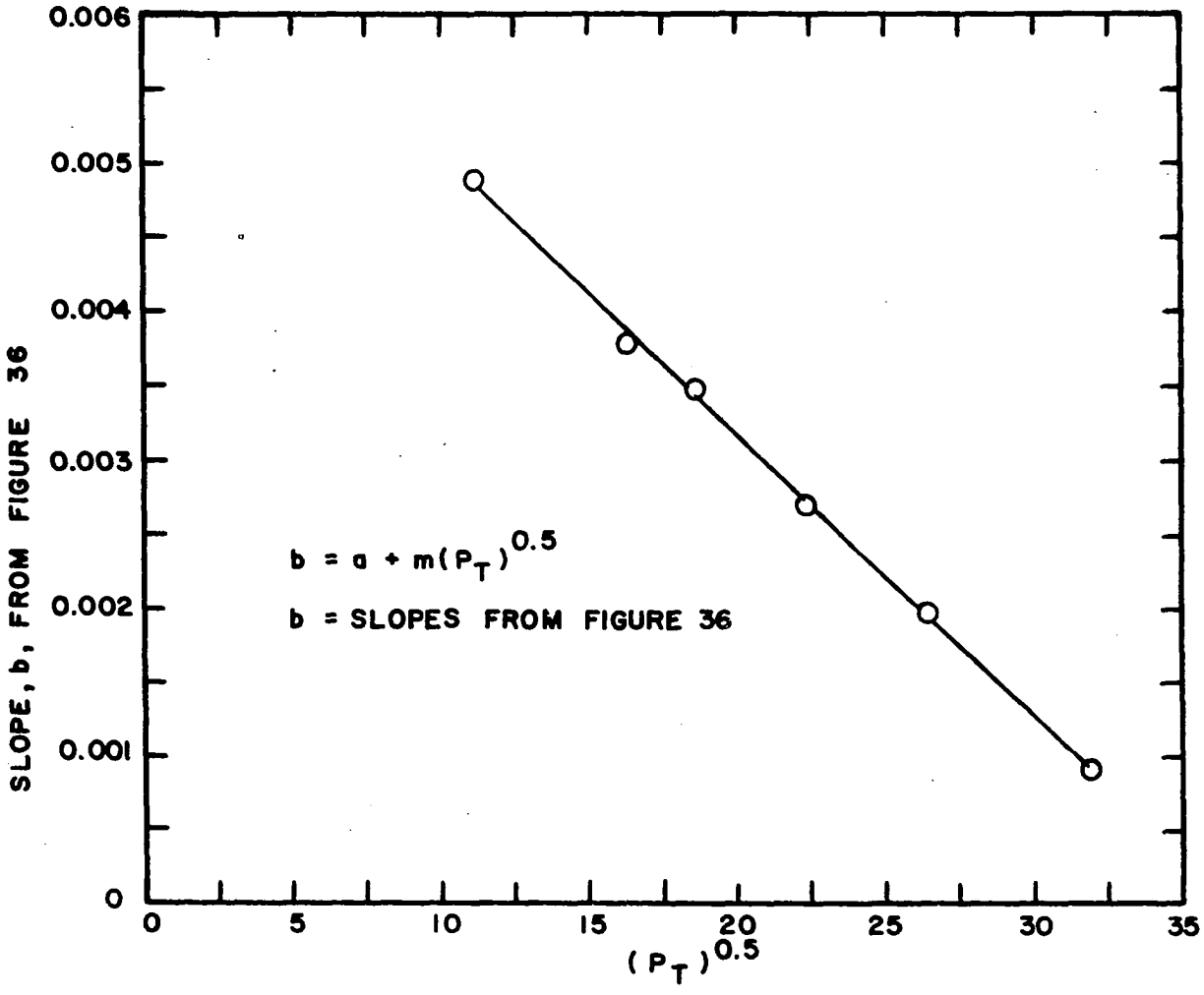

FIGURE 37 SLOPE, b, VS. $(P_T)^{0.5}$ FOR C_1 - nC_4 MIXTURES

The straight line of Figure 33 may be expressed mathematically as:

$$1/X_T = 737.6 - 3360(K_{ADS})^{0.5} \quad (45)$$

or,
$$1/X_T = 737.6 - 3360\ (y/x)^{0.5} \quad (46)$$

where x, as shown in Figure 32, can be expressed as:

$$x = 0.01684 + 20.84y. \quad (47)$$

Another correlation of the Freundlich type can be seen from Figure 35, of the type:

$$v_4 = k'P_4^{1/n}\ , \quad (48)$$

but again, as with the previous correlation, numerous such correlations would be necessary to define a wide pressure range or to develop further correlations with total pressure of the system. While such correlations may be easily used for most engineering calculations, and seem to be within determination from this experimental investigation, they again seem redundant in light of the simplicity and theoretical soundness of the monolayer isotherm presented previously. Furthermore, such empirical correlations do not readily illuminate the underlying model of adsorption.

Another correlation with partial pressure is suggested by examination of Figure 36. Figure 37 is a plot of the slopes of each total pressure curve in Figure 36. The straight lines in Figure 36 can be expressed as:

$$v_4 = a + bP_4\ , \quad (49)$$

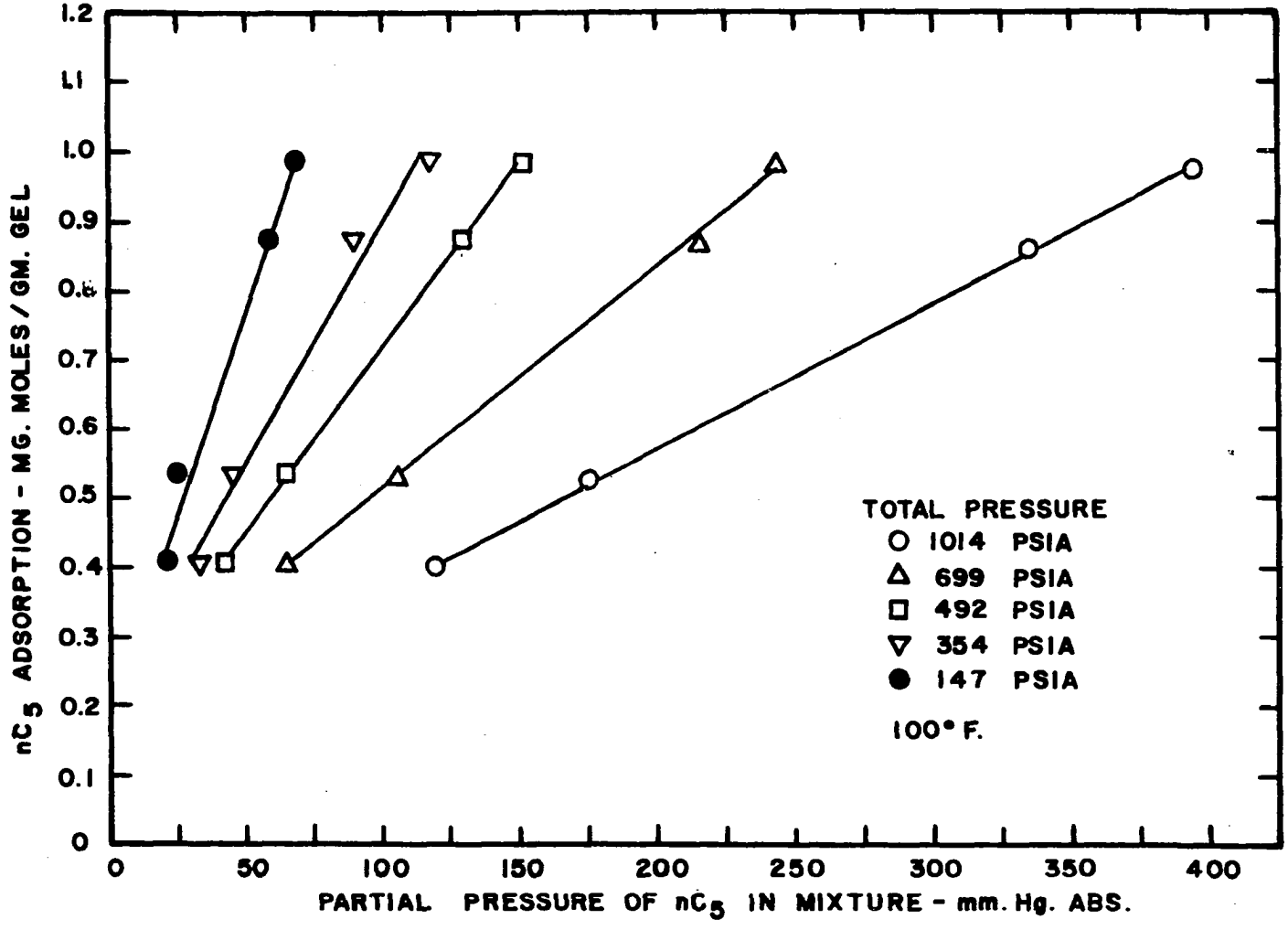

FIGURE 38 EFFECT OF PARTIAL PRESSURE OF nC_5 ON ADSORPTION FROM C_1 - nC_5 MIXTURES

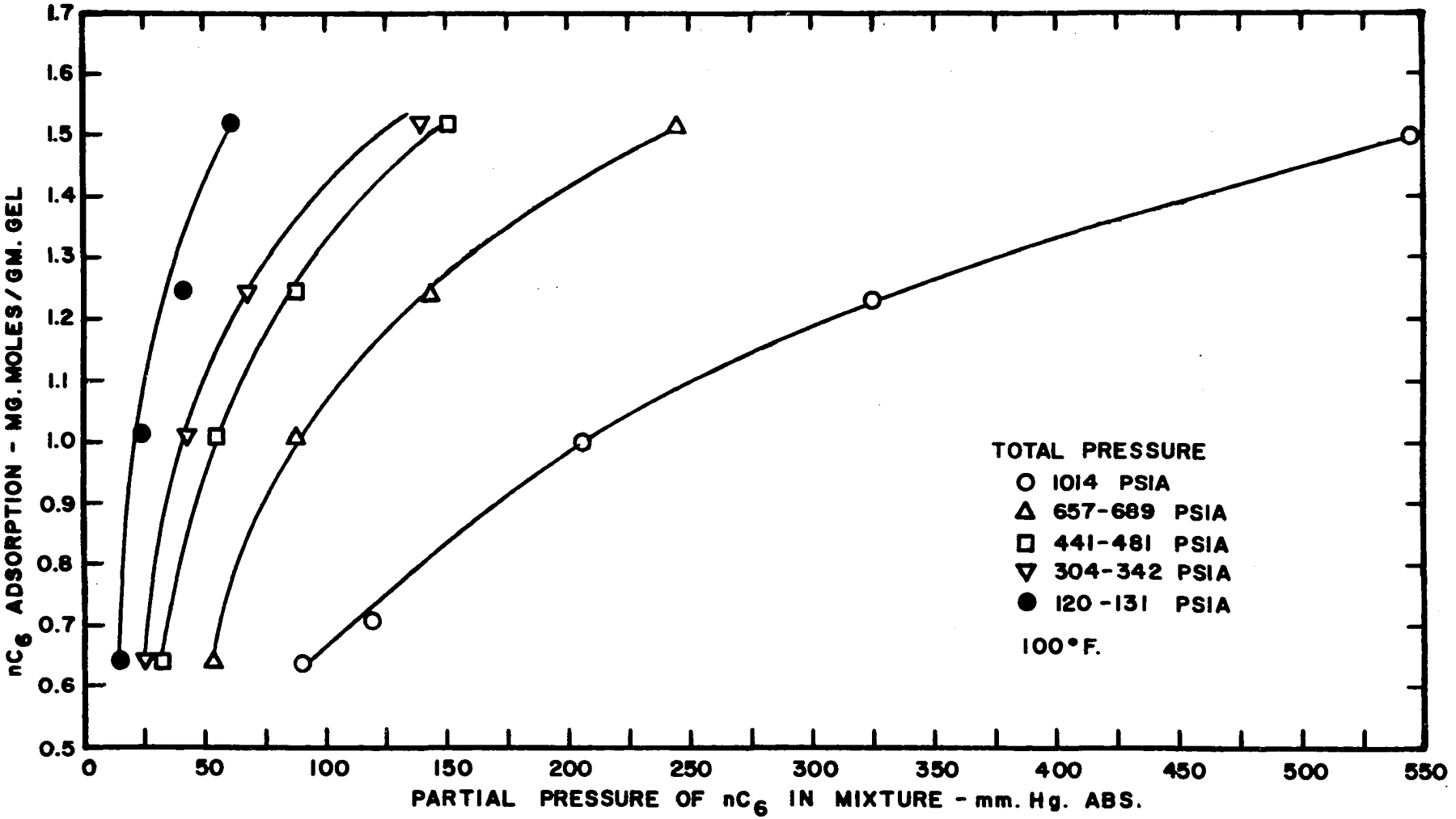

FIGURE 39 EFFECT OF PARTIAL PRESSURE OF nC_6 ON ADSORPTION FROM $C_1 - nC_6$ MIXTURES

where the slope, b, may be expressed as a function of the total system pressure, by the relationship:

$$b = 0.007 - 0.00019\ (P_T)^{0.5} \tag{50}$$

such that the empirical adsorption correlation with partial pressure becomes:

$$v_4 = 0.04 + 0.362P_4 - (0.000982P_T^{0.5})\ P_4\ . \tag{51}$$

This equation satisfactorily reproduces the experimental data for the n-butane system at all pressure levels. However, as was mentioned before, the underlying physical model of adsorption is not apparent from the empirical isotherm, and the extension of such an equation to prediction of ternary mixtures has not been established. Such a correlation is also suggested for the n-pentane-methane binaries by Figure 38, but Figure 39 does not indicate that such a simple correlation could be found to fit the experimental n-hexane data.

Comparison with other Reported Results

The data of Mason and Cooke (30) were obtained in systems basically identical to those used in these experiments, i.e., involved adsorption isotherms at 100° F. on Davison 03 grade silica gel, using Phillips Pure Grade hydrocarbons. However, when the results of these two works are compared, as shown in Figure 11, quite large differences were noted. Mason and Cooke show considerably greater adsorptive capabilities than the results of this work, and even greater in some instances than the adsorption calculated from the BET equation assuming 2 and 3 layers of adsorption.

It is believed that the discrepancies in these two works lie in the manner in which the binary mixture results of Mason and Cooke were obtained. The pure component data were obtained by straightforward volumetric methods in which the actual adsorption could be measured. There is no doubt or question as to the validity of their pure component data and they were incorporated into the correlations of the present work, thereby foregoing the necessity for making further pure component runs in the work reported herein.

Mason and Cooke's mixture data were obtained by a continuous flow method described by Eberly (18), in which the adsorbent is initially saturated with the hydrocarbon component of interest and a desorption breakout curve is then obtained by continuously flowing a stream of non-adsorbable carrier gas through the bed. The adsorbed material is eluted by the pure carrier gas alone. According to this method, the quantity of material adsorbed is determined by evaluating the appropriate areas under the desorption curve of concentration versus time or quantity of pure carrier gas injected. This method necessarily assumes that diffusional effects in the flowing stream of adsorbate and carrier are negligible, and that instantaneous equilibrium is established between the gaseous and adsorbed phases. No real issue is taken with the Eberly method provided a non-adsorbable carrier gas is used and the assumption of instantaneous equilibrium applies. Mason and Cooke's results were calculated according to the Eberly method, and it is seriously doubted that the condition of instantaneous equilibrium could have been met in their work, although it would be most difficult, if not impossible, to determine just how far removed from

that assumption their results may have been. The departure from the assumption of instantaneous equilibrium would have the effect of increasing the calculated adsorption for any given composition. Thus, it is believed that the mixture data of Mason and Cooke may be in error due to the manner in which they were obtained. The results reported in the present investigation are believed to be the more accurate and seem to constitute the only reliable mixture data available for direct application to the adsorption of hydrocarbon components of interest in 03 type silica gel systems.

Comparison of Static and Dynamic Data

Another objective of this experimental work was to determine the relationship, if any, between the static equilibria and available dynamic adsorption data. Figures 40 and 41 are plots of n-pentane and n-hexane comparisons, respectively. The dynamic data points are those obtained from dynamic adsorption tests at the University of Oklahoma Natural Gas Research Laboratory for hydrocarbon - 03 silica gel systems. Although insufficient information is available to develop a direct correlation, the two figures indicate that the values of pentane and hexane adsorption obtained in this work are reasonable and compatible with the dynamic results, further substantiating the previous contention that the present work was more accurate than that presented by Mason and Cooke. Due to the scatter of the dynamic results with velocity of flow through the bed, it appears that the static equilibria data and the prediction technique confirmed herein may be used with some degree of confidence in predicting values

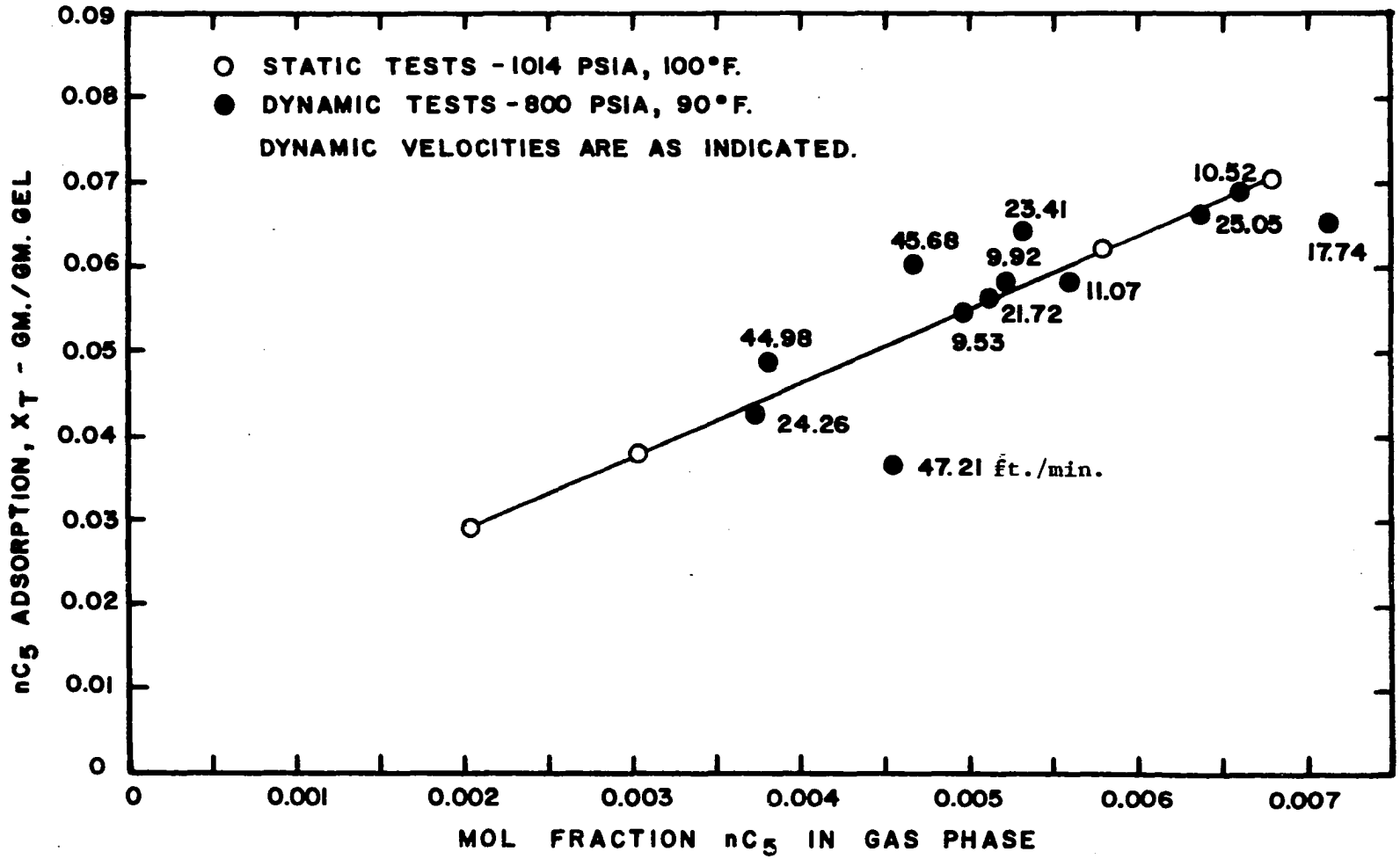

FIGURE 40 COMPARISON OF STATIC AND DYNAMIC ADSORPTION OF nC_5 FROM C_1 - nC_5 MIXTURES

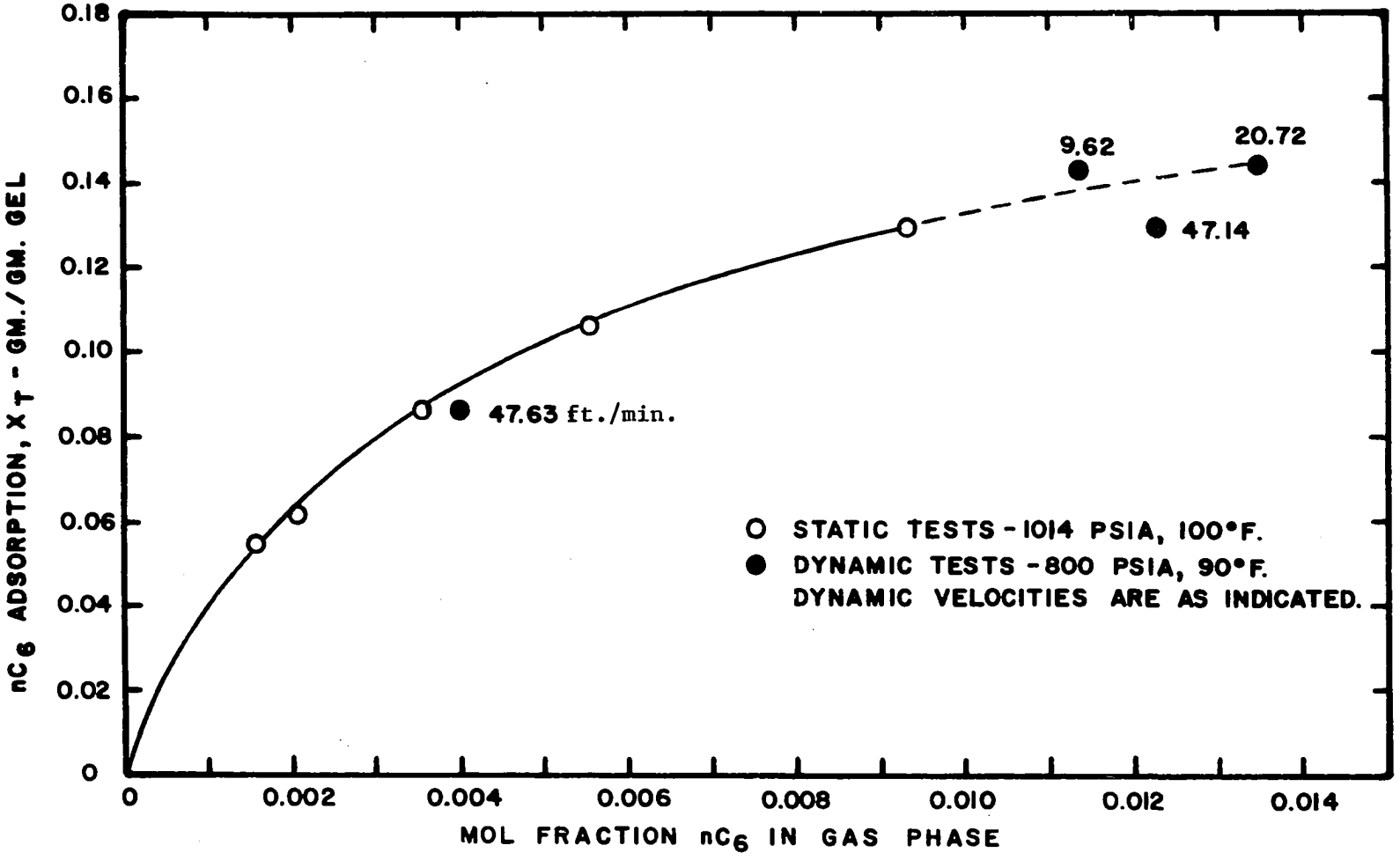

FIGURE 41 COMPARISON OF STATIC AND DYNAMIC ADSORPTION OF nC_6 FROM C_1 - nC_6 MIXTURES

of X_T for adsorber design purposes.

Summary

This study contributes practical and meaningful information to a better understanding of adsorption behavior in systems of 03 silica gel and hydrocarbon gas mixtures. These results should help the engineer to better design commercial adsorption units in the petroleum industry.

The results presented herein show rather conclusively that the adsorption of hydrocarbon gas mixtures on 03 grade silica gels were satisfactorily correlated, and may be so predicted in future work, by application of a monolayer adsorption theory. This theory was a special modification of the BET theory for the case of one layer of adsorbed molecules, but with fugacities substituted for pressures to account for the non-ideality of the adsorbed phase.

Other empirical correlations have been drawn, but they are not as useful nor do they contribute as much to the understanding of the adsorption phenomenon as does the monolayer correlation discussed above.

It is concluded from these results that useful values of X_T, the maximum adsorptive capacity, can be readily and easily obtained from this correlation technique for use in future design calculations.

CHAPTER VI

CONCLUSIONS

The experimental results presented herein have led to the following specific conclusions:

1. The experimental results were correlated with a modification of the BET equation for one monolayer, which is essentially the Langmuir isotherm, with pressures replaced by fugacities to correct for non-ideality. The experimental results showed excellent agreement with the predicted values at all pressure levels and concentrations, thereby establishing the validity of the adsorption model.
2. The prediction technique developed from binary data was most satisfactorily extended to ternary mixtures, further substantiating the validity of the adsorption model.
3. The static equilibrium results were in excellent agreement with dynamic adsorption results and indicate that equilibrium data may be used to approximate values of adsorption, X_T, to be used in design calculations.

4. The experimental data and results are believed to be the only reliable data available for application to 03 type silica gels, under conditions approximating those of these experiments.
5. The experimental technique and procedure, as outlined, is a reasonably simple, rapid, and sound means of obtaining equilibrium data on hydrocarbon gas mixtures.
6. The experimental data and results have accomplished the objectives outlined at the outset and should provide useful tools in adsorption design and evaluation work.

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APPENDIX A

PREDICTION TECHNIQUE

OUTLINE OF CALCULATION PROCEDURE

The prediction technique and calculation procedure referred to in the text was a modification of the BET treatment given by Hill (7,8) and Mason and Cooke (30). For this work, however, the procedure is restricted to the monolayer case where n = 1. It is believed that this technique may be used in future design calculations to determine maximum adsorptive capacities of 03 type silica gels. The remarkably good results for ternary gas mixtures in this work suggests that the technique may well be extended to other multicomponent mixtures.

The calculation procedure may be outlined as follows:

1. It is first necessary to determine the vapor fugacities for each component in the mixture, which at equilibrium will be equal to the fugacities in the adsorbed phase. The fugacities may be determined by application of the Benedict-Webb-Rubin equation of state or by use of the Edmister charts, reproduced here as Figures 7-9. The constant θ^V for each component may be determined from Figure 7 for methane or Figure 8 for hydrocarbon vapor mixtures. The term B_r for each component is defined as the molal average boiling point of the mixture divided by the individual component boiling points. The fugacity may then be determined from Figure 9.
2. Calculate the $x_i c_i$ values for each component in the

mixture, using Equation 35. The BET constants are tabulated in Table 1.

3. The value of E_o, given in Equation 34, may be obtained by summing the individual $x_i c_i$ values.
4. Calculate the individual N_{il} values for each component by Equation 38.
5. Calculate the individual γ_{il} values for each component by Equation 39.
6. Then the adsorption, v_i, may be determined by using Equation 44. The value of v_m must be known from pure component data. For 03 type silica gels, the value of v_m may be determined from Table 1 for gels having surface areas identical to that reported in the table. For other surface areas, these values of v_m may be corrected by a ratio of the surface areas.

As concluded previously, this calculation technique gave excellent agreement with the experimental adsorption results. It is not concluded, however, that these results could be further extended to systems containing gels differing from the 03 type silica gel used in this study. If the values of the BET constant and monolayer adsorption capacities, v_m, for other gels are known, or can be determined, then the technique outlined above should be equally as applicable as for this study.

APPENDIX B

TABLES

TABLE 1

BET CONSTANTS FOR PURE GASES
[FROM MASON AND COOKE (30)]

Component	c	v_m	v_m^*	f°, Psia	A, $Å^2$/Molecule
C_1	10.7	2.75	2.65	3926	50.1
nC_4	11.3	2.39	2.302	47.2	57.6
nC_5	12.1	2.18	2.10	14.7	63.2
nC_6	12.3	1.97	1.90	4.9	68.8

*Values corrected for differences in apparent surface areas of gel. These values are for 800 m^2/gm.

TABLE 2

SUMMARY OF RESULTS - C_1-nC_5-nC_6 TERNARIES

EQ. TEMP. = 100°F

Eq. Pressure, Psia	Mol Fraction In Gas Phase		Exp. Adsorption Mg. Moles/Gm. Gel		Calc. Adsorption Mg. Moles/Gm. Gel		Per Cent Difference	
	nC_5	nC_6	nC_5	nC_6	nC_5	nC_6	nC_5	nC_6
Run 16								
1014.3	0.00505	0.00154	0.588	0.401	0.586	0.4225	-0.34	+5.36
662.3	0.00541	0.00147	0.592	0.404	0.647	0.442	+9.29	+9.40
436.3	0.00506	0.00122	0.595	0.405	0.641	0.414	+7.73	+2.22
Run 17								
1014.2	0.00550	0.00381	0.459	0.709	0.470	0.768	+2.4	+8.32
662.2	0.00543	0.00330	0.465	0.715	0.502	0.765	+7.95	+7.0
436.2	0.00525	0.00308	0.467	0.717	0.490	0.771	+4.93	+7.53
Run 18								
1014.2	0.00540	0.00287	0.491	0.635	0.514	0.647	+4.68	+1.89
662.2	0.00523	0.00266	0.497	0.638	0.530	0.677	+6.65	+6.11
436.2	0.00498	0.00222	0.499	0.641	0.536	0.657	+7.42	+2.5

TABLE 3

PRIMARY ADSORPTION DATA - BINARIES
EQ. TEMP. = 100°F

Run	Peq. Psia	Gms. Gas Injected		Gms. Gas In Dead Volume		Y_4 In Dead Vol.	Gms. Gas Removed		Gms. Gas Adsorbed	
		C_1	nC_4	C_1	nC_4		C_1	nC_4	C_1	nC_4
1	1014.0	2.454	0.1529	1.0190	0.0063	0.00170	0.5869	0.0000	0.8481	0.1466
2	1014.2	8.9745	0.3730	1.0160	0.0170	0.00459	7.2774	0.0146	0.6811	0.3414
3	1014.1	6.5530	0.4423	1.0155	0.0213	0.00575	4.7873	0.0089	0.7502	0.4121
4	1019.0	4.350	0.6158	1.0195	0.0298	0.00800	2.6890	0.0277	0.6415	0.5583
5	1014.0	6.508	0.9122	1.0130	0.0445	0.01199	4.8870	0.0716	0.6080	0.7960
6	1014.2	11.241	1.7158	1.0070	0.0804	0.02158	9.7970	0.2508	0.4370	1.3846
7	1014.3	25.290	1.5500	1.0110	0.0637	0.01710	23.800	0.3684	0.4790	1.1180

Run	Peq.	C_1	nC_4	C_1	nC_5	Y_5	C_1	nC_5	C_1	nC_5
8	1014.2	27.600	1.7190	1.0160	0.0312	0.00679	26.250	0.3082	0.3340	1.3796
9	1014.3	9.356	0.7600	1.0170	0.0140	0.00304	7.806	0.0000	0.5330	0.7461
10	1014.3	9.700	0.5783	1.0180	0.0094	0.00205	8.0283	0.0000	0.6737	0.5689
11	1014.3	18.690	1.2746	1.0180	0.0266	0.00579	17.290	0.0272	0.3820	1.2208

TABLE 3--Continued

Run	Peq. Psia	Gms. Gas Injected		Gms. Gas In Dead Volume		Y_6 In Dead Vol.	Gms. Gas Removed		Gms. Gas Adsorbed	
		C_1	nC_6	C_1	nC_6		C_1	nC_6	C_1	nC_6
12	1014.2	28.730	1.0850	1.0180	0.0086	0.00157	27.055	0.000	0.6570	1.0764
13	1014.3	29.450	1.2120	1.0170	0.0130	0.00206	27.772	0.000	0.6610	1.1990
13	1014.3	53.99	2.2620	1.0180	0.0307	0.00558	52.464	0.1478	0.5078	2.0835
14	1014.1	43.780	1.7404	1.0180	0.0196	0.00356	41.480	0.0268	0.7584	1.6940
15	1014.2	48.920	2.620	1.0170	0.0514	0.00932	48.089	0.0315	-	2.5371

TABLE 4

PRIMARY DESORPTION DATA - BINARIES
EQ. TEMP. = 100°F

Peq. Psia	Mol Fraction nC_4 In Dead Vol.	Gms. Gas In Dead Volume		Gms. Gas Displaced		Gms. Gas Adsorbed	
		C_1	nC_4	C_1	nC_4	C_1	nC_4
		Run 1 - C_1-nC_4 Mixture					
694.2	0.00145	0.6746	0.0035	0.4487	0.0015	0.7438	0.1479
		Run 2 - C_1-nC_4 Mixture					
704.1	0.00365	0.6826	0.0091	0.3983	0.0018	0.6163	0.3475
509.1	0.00320	0.4840	0.0056	0.3190	0.0011	0.4959	0.3497
370.1	0.00373	0.3469	0.0047	0.1695	0.0005	0.4635	0.3501
269.1	0.00379	0.2496	0.0034	0.2389	0.0013	0.3219	0.3501
131.1	0.00532	0.1199	0.0023	0.2681	0.0019	0.1835	0.3493
66.6	0.00812	0.0604	0.0018	0.1379	0.0022	0.1051	0.3477
		Run 3 - C_1-nC_4 Mixture					
705.1	0.00423	0.6854	0.0106	0.4855	0.0045	0.5948	0.4184
509.1	0.00472	0.4840	0.0083	0.3191	0.0009	0.4771	0.4197
370.1	0.00478	0.3462	0.0060	0.1988	0.0012	0.4161	0.4208
269.0	0.00491	0.2491	0.0045	0.1800	0.0010	0.3332	0.4214
125.0	0.00650	0.1142	0.0027	0.2871	0.0032	0.1810	0.4199
66.0	0.01097	0.0596	0.0024	0.1370	0.0030	0.0986	0.4172

TABLE 4--Continued

Run 4 - C_1-nC_4 Mixture

Peq. Psia	Mol Fraction nC_4 In Dead Vol.	Gms. Gas In Dead Volume		Gms. Gas Displaced		Gms. Gas Adsorbed	
		C_1	nC_4	C_1	nC_4	C_1	nC_4
694.0	0.00621	0.6720	0.0152	0.4550	0.0049	0.5340	0.5679
492.0	0.00668	0.4662	0.0114	0.2970	0.0030	0.4428	0.5688
354.0	0.00642	0.3304	0.0077	0.2373	0.0026	0.3413	0.5698
261.0	0.00638	0.2412	0.0056	0.1483	0.0017	0.2822	0.5703
119.0	0.01051	0.1081	0.0042	0.2833	0.0067	0.1320	0.5650
66.0	0.01546	0.0594	0.0034	0.1349	0.0051	0.0458	0.5608

Run 5 - C_1-nC_4 Mixture

699.0	0.01261	0.6746	0.0312	0.4172	0.0026	0.5292	0.8067
497.0	0.00915	0.4690	0.0157	0.3173	0.0126	0.4175	0.8096
354.0	0.00982	0.3292	0.0118	0.1952	0.0048	0.3621	0.8090
261.0	0.01040	0.2402	0.0092	0.1657	0.0042	0.2854	0.8072
119.2	0.01654	0.1077	0.0066	0.2775	0.0126	0.1404	0.7972
60.2	0.03076	0.0534	0.0061	0.1571	0.0130	0.0376	0.7846

TABLE 4--Continued

Run 6 - C_1-nC_4 Mixture

Peq. Psia	Mol Fraction nC_4 In Dead Vol.	Gms. Gas In Dead Volume		Gms. Gas Displaced		Gms. Gas Adsorbed	
		C_1	nC_4	C_1	nC_4	C_1	nC_4
694.1	0.01583	0.6684	0.0390	0.4140	0.0160	0.3616	1.4101
486.1	0.01662	0.4564	0.0279	0.3250	0.0150	0.2486	1.4061
342.1	0.01852	0.3157	0.0217	0.1996	0.0104	0.1897	1.4021
244.1	0.02180	0.2222	0.0179	0.1515	0.0085	0.1317	1.3973
108.1	0.03670	0.0958	0.0132	0.2524	0.0275	0.0057	1.3745
54.1	0.06360	0.0463	0.0114	0.1061	0.0239	-0.0509	1.3524

Run 8 - C_1-nC_5 Mixture

Peq. Psia	Mol Fraction nC_5 In Dead Vol.	Gms. Gas In Dead Volume		Gms. Gas Displaced		Gms. Gas Adsorbed	
		C_1	nC_5	C_1	nC_5	C_1	nC_5
699.2	0.00625	0.6775	0.0192	0.4084	0.0016	0.2641	1.3900
492.2	0.00568	0.4670	0.0120	0.3187	0.0013	0.1559	1.3959
354.2	0.00620	0.3316	0.0093	0.2189	0.0011	0.0724	1.3975
147.2	0.00876	0.1343	0.0054	0.3369	0.0031	-0.0672	1.3984

TABLE 4--Continued

Peq. Psia	Mol Fraction nC_5 In Dead Vol.	Gms. Gas In Dead Volume		Gms. Gas Displaced		Gms. Gas Adsorbed	
		C_1	nC_5	C_1	nC_5	C_1	nC_5
Run 9 - C_1-nC_5 Mixture							
699.3	0.00274	0.6795	0.0084	0.4492	0.0008	0.4213	0.7509
492.3	0.00239	0.4675	0.0050	0.3095	0.0005	0.3238	0.7538
354.3	0.00240	0.3326	0.0036	0.2298	0.0002	0.2289	0.7550
147.3	0.00371	0.1351	0.0023	0.3700	0.0000	0.0564	0.7563
Run 10 - C_1-nC_5 Mixture							
699.3	0.00167	0.6800	0.0051	0.4298	0.0002	0.5819	0.5730
492.3	0.00160	0.4680	0.0034	0.3098	0.0002	0.4841	0.5745
354.3	0.00175	0.3326	0.0026	0.2200	0.0000	0.3995	0.5753
147.3	0.00294	0.1351	0.0018	0.3967	0.0033	0.2103	0.5728
Run 11 -C_1-nC_5 Mixture							
699.3	0.00557	0.6790	0.0171	0.4190	0.0010	0.3020	1.2293
492.3	0.00483	0.4670	0.0102	0.2897	0.0003	0.2243	1.2359
354.3	0.00475	0.3316	0.0071	0.2294	0.0006	0.1303	1.2384
147.3	0.00755	0.1348	0.0046	0.3479	0.0021	-0.0208	1.2389

TABLE 4--Continued

Run 12 - C_1-nC_6 Mixture

Peq. Psia	Mol Fraction nC_6 In Dead Vol.	Gms. Gas In Dead Volume		Gms. Gas Displaced		Gms. Gas Adsorbed	
		C_1	nC_6	C_1	nC_6	C_1	nC_6
689.2	0.00139	0.6680	0.0050	0.420	0.000	0.5870	1.0800
481.2	0.00124	0.4575	0.0031	0.290	0.000	0.5075	1.0819
342.2	0.00139	0.3206	0.0024	0.210	0.000	0.4344	1.0826
131.2	0.00210	0.1207	0.0014	0.390	0.000	0.2443	1.0836

Run 13 C_1-nC_6 Mixture

673.3	0.00386	0.6505	0.0136	0.410	0.000	0.4653	2.1006
447.3	0.00363	0.4225	0.0083	0.290	0.000	0.4033	2.1059
310.3	0.00411	0.2890	0.0064	0.220	0.000	0.3168	2.1078
120.3	0.00664	0.1099	0.0040	0.290	0.000	0.2059	2.1102

Run 14 - C_1-nC_6 Mixture

657.1	0.00242	0.6360	0.0083	0.430	0.000	0.7104	1.7053
441.1	0.00233	0.4170	0.0052	0.280	0.000	0.6494	1.7084
304.1	0.00265	0.2834	0.0025	0.190	0.000	0.5930	1.7111
120.1	0.00370	0.1100	0.0022	0.280	0.000	0.4864	1.7114

TABLE 4--Continued

Run 15 - C_1-nC_6 Mixture							
Peq. Psia	Mol Fraction nC_5 In Dead Vol.	Gms. Gas In Dead Volume		Gms. Gas Displaced		Gms. Gas Adsorbed	
		C_1	nC_6	C_1	nC_6	C_1	nC_6
657.2	0.00675	0.6340	0.0232	0.4273	0.0027	-	2.5626
441.2	0.00634	0.4160	0.0142	0.2886	0.0014	-	2.5702
304.2	0.00861	0.2816	0.0132	0.1795	0.0005	-	2.5707
120.2	0.00971	0.1092	0.0058	0.2877	0.0023	-	2.5758

TABLE 5

PRIMARY ADSORPTION DATA - TERNARIES
EQ. TEMP. = 100°F

Run	Peq. Psia	Mol Fraction In Dead Volume		Gms. Gas Injected			Gms. Gas In Dead Vol.		
		nC_5	nC_6	C_1	nC_5	nC_6	C_1	nC_5	nC_6
16	1014.3	0.00505	0.00154	28.980	1.317	0.688	1.017	0.0233	0.0085
17	1014.2	0.00550	0.00381	29.400	1.114	1.221	1.013	0.0253	0.0209
18	1014.2	0.00540	0.00287	28.460	1.089	1.190	1.016	0.0158	0.0249

Run	Gms. Gas Displaced			Gms. Gas Adsorbed		
	C_1	nC_5	nC_6	C_1	nC_5	nC_6
16	26.8160	0.4590	0.0	1.1470	0.8347	0.6795
17	27.4975	0.4375	0.0	0.8895	0.6512	1.200
18	26.570	0.4690	0.0	0.8740	0.6961	1.0732

TABLE 6

PRIMARY DESORPTION DATA - TERNARIES
EQ. TEMP. = 100°F

Peq. Psia	Mol Fraction In Dead Volume		Gms. Gas In Dead Volume		Gms. Gas Displaced		Gms. Gas Adsorbed	
	nC_5	nC_6	nC_5	nC_6	nC_5	nC_6	nC_5	nC_6
Run 16 - C_1-nC_5-nC_6 Mixture								
662.3	0.00541	0.00147	0.0156	0.0051	0.0037	0	0.8387	0.6829
436.3	0.00506	0.00122	0.0094	0.0027	0.0021	0	0.8428	0.6853
Run 17 - C_1-nC_5-nC_6 Mixture								
662.2	0.00543	0.00330	0.0157	0.0114	0.0028	0	0.6580	1.2095
436.2	0.00525	0.00308	0.0098	0.0068	0.0017	0	0.6622	1.2141
Run 18 - C_1-nC_5-nC_6 Mixture								
662.2	0.00523	0.00266	0.0149	0.0092	0.0027	0	0.7034	1.0798
436.2	0.00498	0.00222	0.0093	0.0049	0.0019	0	0.7071	1.0841

TABLE 7

SUMMARY OF RESULTS - C_1-nC_4 BINARIES

EQ. TEMP. = 100°F

Peq. Psia	y_4	v_l Mg. Moles / Gm. Gel	v_4 Mg. Moles / Gm. Gel	v Mg. Moles / Gm. Gel	X_T Gms./Gm. Gel	x_4	Z_t	P_4 mm.Hg.
			Run 1					
1014.0	0.00170	2.696	0.1284	2.8244	0.00746	0.0455	0.905	98.5
694.2	0.00145	2.361	0.1296	2.4906	0.00753	0.052	0.934	55.8
			Run 2					
1014.2	0.00459	2.162	0.2992	2.4612	0.01739	0.1216	0.903	266.6
704.1	0.00365	1.958	0.3046	2.2626	0.01770	0.1347	0.934	142.2
509.1	0.00320	1.574	0.3063	1.8803	0.01781	0.1630	0.953	88.4
370.1	0.00373	1.471	0.3068	1.7778	0.01783	0.1727	0.967	73.8
269.1	0.00379	1.021	0.3070	1.3280	0.01784	0.2310	0.977	54.0
131.1	0.00532	0.582	0.3061	0.8881	0.01780	0.3446	0.989	36.5
66.6	0.00812	0.3333	0.3048	0.6381	0.01771	0.4780	0.995	28.1

TABLE 7--Continued

Peq. Psia	y_4	v_1 Mg. Moles / Gm. Gel	v_4 Mg. Moles / Gm. Gel	v Mg. Moles / Gm. Gel	X_T Gms./Gm. Gel	x_4	Z_t	P_4 mm.Hg.
Run 3								
1014.1	0.00575	2.381	0.3611	2.7421	0.0210	0.1317	0.903	334.0
705.1	0.00423	1.888	0.3667	2.2547	0.02131	0.1628	0.931	165.6
509.1	0.00472	1.515	0.3677	1.8827	0.02137	0.1951	0.952	130.5
370.1	0.00478	1.321	0.3687	1.6897	0.02141	0.218	0.966	94.7
269.0	0.00491	1.058	0.3692	1.4272	0.02146	0.2586	0.977	69.9
125.0	0.00650	0.5744	0.3680	0.9424	0.02139	0.3904	0.989	42.5
66.0	0.01097	0.3130	0.3658	0.6788	0.02125	0.5390	0.995	37.7
Run 4								
1019.0	0.0080	2.038	0.4892	2.5272	0.02843	0.1937	0.901	468.0
694.0	0.00621	1.696	0.4977	2.1937	0.02891	0.2270	0.933	239.0
492.0	0.00668	1.405	0.4985	1.9035	0.02898	0.2618	0.953	178.3
354.0	0.00642	1.083	0.4992	1.5822	0.02901	0.3154	0.968	121.4
261.0	0.00638	0.896	0.4999	1.3959	0.02903	0.3582	0.977	88.1
119.0	0.01051	0.419	0.4950	0.9140	0.02878	0.5420	0.990	64.8
66.0	0.01546	0.1453	0.4912	0.6365	0.02854	0.7710	0.994	53.1

TABLE 7--Continued

Peq. Psia	y_4	v_1 Mg. Moles / Gm. Gel	v_4 Mg. Moles / Gm. Gel	v Mg. Moles / Gm. Gel	X_T Gms./Gm. Gel	x_4	Z_t	P_4 mm.Hg.
			Run 5					
1014.0	0.01199	1.931	0.6978	2.6288	0.04053	0.2656	0.899	699
699.0	0.01261	1.680	0.7066	2.3866	0.04109	0.2960	0.930	490
497.0	0.00915	1.326	0.7092	2.0352	0.04121	0.3480	C 954	246.4
354.0	0.00982	1.150	0.7086	1.8586	0.04120	0.3814	0.968	184.6
261.0	0.01040	0.9062	0.7072	1.6134	0.04110	0.4380	0.977	143.6
119.2	0.01654	0.4458	0.6982	1.1440	0.04060	0.6100	0.989	103
60.2	0.03076	0.1194	0.6876	0.8070	0.03998	0.8520	0.993	96.5
			Run 6					
1014.2	0.02158	1.387	1.213	2.600	0.07046	0.467	0.896	1262
694.1	0.01583	1.148	1.235	2.383	0.07180	0.518	0.929	611.4
486.1	0.01662	0.7892	1.232	2.0212	0.07160	0.610	0.952	438.7
342.1	0.01852	0.6020	1.229	1.831	0.07142	0.671	0.967	338.8
244.1	0.02180	0.4180	1.225	1.643	0.07118	0.745	0.977	281.6
108.1	0.03670	0.0181	1.204	1.2221	0.0700	0.986	0.988	207.5
54.1	0.06360	-	1.185	1.185	0.06884	1.0	0.994	172.9
			Run 7					
1014.3	0.0171	1.520	0.979	2.499	0.0569	0.392	0.896	1014

TABLE 8

SUMMARY OF RESULTS - C_1-nC_5 BINARIES

EQ. TEMP. = 100°F

Peq. Psia	y_5	v_1 Mg. Moles / Gm. Gel	v_5 Mg. Moles / Gm. Gel	v Mg. Moles / Gm. Gel	X_T Gms./Gm. Gel	x_5	Z_t	P_5 mm.Hg.
Run 8								
1014.2	0.00679	1.060	0.9725	2.0325	0.0702	0.479	0.902	394.6
699.2	0.00625	0.8375	0.980	1.8175	0.07075	0.540	0.932	242.6
492.2	0.00568	0.4940	0.983	1.477	0.0710	0.666	0.954	151.5
354.2	0.00620	0.2296	0.985	1.2146	0.0711	0.811	0.968	117.4
147.2	0.00876	-0.2130	0.985	0.7720	0.0711	1.00	0.988	67.6
Run 9								
1014.3	0.00304	1.690	0.5264	2.2164	0.03799	0.2374	0.904	176.4
699.3	0.00274	1.335	0.529	1.8640	0.03822	0.2838	0.934	106.1
492.3	0.00239	1.027	0.532	1.5590	0.03838	0.3414	0.954	63.9
354.3	0.00240	0.726	0.5325	1.2585	0.03842	0.4230	0.968	44.1
147.3	0.00371	0.1791	0.5325	0.7116	0.03846	0.7480	0.988	24.0

TABLE 8--Continued

Peq. Psia	y_5	v_1 Mg. Moles / Gm. Gel	v_5 Mg. Moles / Gm. Gel	v Mg. Moles / Gm. Gel	X_T Gms./Gm. Gel	x_5	Z_t	P_5 mm.Hg.
Run 10								
1014.3	0.00205	2.136	0.401	2.537	0.02896	0.158	0.905	118.9
699.3	0.00167	1.848	0.404	2.252	0.02918	0.1795	0.934	64.7
492.3	0.00160	1.536	0.405	1.941	0.02922	0.2086	0.954	42.7
354.3	0.00175	1.269	0.406	1.675	0.02930	0.2422	0.968	33.1
147.3	0.00294	0.667	0.404	1.071	0.02916	0.377	0.988	22.6
Run 11								
1014.3	0.00579	1.211	0.861	2.072	0.0621	0.416	0.903	336
699.3	0.00557	0.958	0.867	1.825	0.06255	0.475	0.932	216.2
492.3	0.00483	0.711	0.871	1.582	0.0629	0.550	0.954	129
354.3	0.00475	0.413	0.873	1.286	0.0630	0.680	0.968	89.8
147.3	0.00755	-0.066	0.873	0.807	0.0630	1.0	0.988	58.1

TABLE 9

SUMMARY OF RESULTS - C_1-nC_6 BINARIES

EQ. TEMP. = 100°F

Peq. Psia	y_6	v_1 Mg. Moles / Gm. Gel	v_6 Mg. Moles / Gm. Gel	v Mg. Moles / Gm. Gel	X_T Gms./Gm. Gel	x_6	Z_t	P_6 mm.Hg.
			Run 12					
1014.2	0.00157	2.084	0.636	2.720	0.0548	0.234	0.904	91.1
689.2	0.00139	1.861	0.639	2.500	0.0550	0.2556	0.936	52.9
481.2	0.00124	1.610	0.6395	2.2495	0.05505	0.2842	0.956	32.3
342.2	0.00139	1.379	0.6395	2.019	0.05505	0.3170	0.970	25.4
131.2	0.00210	0.775	0.640	1.415	0.0551	0.4525	0.989	14.4
			Run 13					
1014.3	0.00206	2.099	0.708	2.807	0.0610	0.2522	0.905	119.4
1014.3	0.00558	1.610	1.230	2.840	0.1060	0.4330	0.901	325.2
673.3	0.00386	1.476	1.240	2.716	0.1069	0.4560	0.937	143.4
447.3	0.00363	1.279	1.242	2.521	0.1071	0.4930	0.960	87.5
310.3	0.00411	1.005	1.244	2.249	0.1072	0.5530	0.973	67.7
120.3	0.00664	0.653	1.245	1.898	0.1073	0.6560	0.99	41.7

TABLE 9--Continued

Peq. Psia	y_6	v_1 Mg. Moles / Gm. Gel	v_6 Mg. Moles / Gm. Gel	v Mg. Moles / Gm. Gel	X_T Gms./Gm. Gel	x_6	Z_t	P_6 mm.Hg.
Run 14								
1014.1	0.00356	2.404	1.000	3.404	0.0862	0.294	0.903	206.6
657.1	0.00242	2.250	1.006	3.256	0.0868	0.3094	0.937	87.6
441.1	0.00233	2.060	1.008	3.068	0.0869	0.3286	0.960	55.3
304.1	0.00265	1.881	1.010	2.891	0.0871	0.3498	0.973	42.8
120.1	0.00370	1.541	1.011	2.552	0.0872	0.3962	0.990	23.2
Run 15								
1014.2	0.00932	-	1.499	-	0.1292	1.0	0.899	544
657.2	0.00675	-	1.512	-	0.1303	1.0	0.936	245
441.2	0.00634	-	1.518	-	0.1308	1.0	0.959	150.8
304.2	0.00861	-	1.518	-	0.1308	1.0	0.973	139
120.2	0.00971	-	1.520	-	0.1311	1.0	0.990	61

TABLE 10

EXPERIMENTAL K VALUES

Peq., Psia	y_4	x_4	$K_4 = y_4/x_4$	$(K_4)^{0.5}$
		Run 1 - C_1-nC_4 Mixture		
1014.0	0.00170	0.0455	0.03736	0.193
694.2	0.00145	0.0520	0.02788	0.1668
		Run 2 - C_1-nC_4 Mixture		
1014.2	0.00459	0.1216	0.03778	0.1942
704.1	0.00365	0.1347	0.02710	0.1646
509.1	0.00320	0.1630	0.01962	0.140
370.1	0.00373	0.1727	0.02160	0.1469
269.1	0.00379	0.2310	0.01640	0.128
131.1	0.00532	0.3446	0.01543	0.1242
66.6	0.00812	0.4780	0.0170	0.1303
		Run 3 - C_1-nC_4 Mixture		
1014.1	0.00575	0.1317	0.0437	0.209
705.1	0.00423	0.1628	0.0260	0.1612
509.1	0.00472	0.1951	0.0242	0.1555
370.1	0.00478	0.2180	0.0219	0.148
269.0	0.00491	0.2586	0.01899	0.1378
125.0	0.00650	0.3904	0.01663	0.129
66.0	0.01097	0.5390	0.02034	0.1425

TABLE 10--Continued

Peq., Psia	y_4	x_4	$K_4 = y_4/x_4$	$(K_4)^{0.5}$
Run 4 - C_1nC_4 Mixture				
1019.0	0.0080	0.1937	0.0413	0.2032
694.0	0.00621	0.2270	0.02736	0.1651
492.0	0.00668	0.2618	0.02552	0.1597
354.0	0.00642	0.3154	0.02034	0.1425
261.0	0.00638	0.3582	0.01780	0.1334
119.0	0.01051	0.5420	0.01940	0.1392
66.0	0.01546	0.7710	0.02004	0.1413
Run 5 - C_1nC_4 Mixture				
1014.0	0.01199	0.2656	0.0451	0.2122
699.0	0.01261	0.2960	0.0426	0.2064
497.0	0.00915	0.3480	0.02628	0.1620
354.0	0.00982	0.3814	0.02574	0.1603
261.0	0.01040	0.4380	0.02376	0.1540
119.2	0.01654	0.610	0.02710	0.1647
60.2	0.03076	0.8520	0.03610	0.190
Run 6 - C_1nC_4 Mixture				
1014.2	0.02158	0.467	0.0462	0.215
694.1	0.01583	0.518	0.03058	0.1748
486.1	0.01662	0.610	0.02724	0.165
342.1	0.01852	0.671	0.0276	0.166
244.1	0.02180	0.745	0.02924	0.171
108.1	0.0367	0.986	0.0372	0.1928
54.1	0.0636	1.0	0.0636	0.252
Run 7 - C_1nC_4 Mixture				
1014.3	0.0171	0.392	0.0436	0.2088

TABLE 10--Continued

Peq., Psia	y_5	x_5	$K_5 = y_5/x_5$	$(K_5)^{0.5}$
Run 8 - C_1nC_5 Mixture				
1014.2	0.00679	0.479	0.01419	0.1190
699.2	0.00625	0.540	0.01158	0.1076
492.2	0.00568	0.666	0.00852	0.0924
354.2	0.00620	0.811	0.00765	0.0869
147.2	0.00876	1.0	0.00876	0.0936
Run 9 - C_1-nC_5 Mixture				
1014.3	0.00304	0.2374	0.01281	0.1131
699.3	0.00274	0.2838	0.00965	0.0982
492.3	0.00239	0.3414	0.0070	0.0837
354.3	0.00240	0.4230	0.00567	0.0753
147.3	0.00371	0.7480	0.00496	0.0705
Run 10 - C_1-nC_5 Mixture				
1014.3	0.00205	0.158	0.01298	0.1139
699.3	0.00167	0.1795	0.0093	0.0965
492.3	0.00160	0.2086	0.00767	0.0875
354.3	0.00175	0.2422	0.00722	0.0850
147.3	0.00294	0.377	0.0078	0.0884
Run 11 - C_1-nC_5 Mixture				
1014.3	0.00579	0.416	0.01393	0.1179
699.3	0.00557	0.475	0.01172	0.1081
492.3	0.00483	0.550	0.00878	0.0937
354.3	0.00475	0.680	0.00699	0.0836
147.3	0.00755	1.0	0.00755	0.0869

TABLE 10--Continued

Peq., Psia	y_6	x_6	$K_6 = y_6/x_6$	$(K_6)^{0.5}$
Run 12 - C_1-nC_6 Mixture				
1014.2	0.00157	0.234	0.00671	0.082
689.2	0.00139	0.2556	0.00544	0.0738
481.2	0.00124	0.2842	0.00436	0.066
342.2	0.00139	0.317	0.00438	0.0662
131.2	0.00210	0.4525	0.00464	0.0681
Run 13 - C_1-nC_6 Mixture				
1014.3	0.00206	0.2522	0.00816	0.0903
1014.3	0.00558	0.433	0.01289	0.1134
673.3	0.00386	0.456	0.00847	0.092
447.3	0.00363	0.493	0.00736	0.0858
310.3	0.00411	0.553	0.00743	0.0863
120.3	0.00664	0.656	0.01011	0.1005
Run 14 - C_1-nC_6 Mixture				
1014.1	0.00356	0.294	0.0121	0.110
657.1	0.00242	0.3094	0.00782	0.0885
441.1	0.00233	0.3286	0.00709	0.0842
304.1	0.00265	0.3498	0.00758	0.0870
120.1	0.00370	0.3962	0.00934	0.0967
Run 15 - C_1-nC_6 Mixture				
1014.2	0.00932	1.0	0.00932	0.0966
657.2	0.00675	1.0	0.00675	0.0822
441.2	0.00634	1.0	0.00634	0.0797
304.2	0.00861	1.0	0.00861	0.0928
120.2	0.00971	1.0	0.00971	0.0986

TABLE 11

n-BUTANE ADSORPTION CALCULATED
BY MONOLAYER BET EQUATION

C_1-nC_4 Mixtures					
	Adsorption, v - Mg. Moles/Gm. Gel				
Mol Fraction n-Butane	P_T = 1014 Psia	P_T = 700 Psia	P_T = 500 Psia	P_T = 360 Psia	P_T = 125 Psia
0.001	0.0855	0.0925	0.0921	0.0868	0.0521
0.003	0.2366	0.2564	0.2528	0.2404	0.1475
0.005	0.3694	0.3972	0.394	0.374	0.234
0.007	0.486	0.519	0.516	0.489	0.312
0.010	0.636	0.675	0.670	0.637	0.419
0.020	0.998	-	-	-	0.70

TABLE 12

n-PENTANE ADSORPTION CALCULATED
BY MONOLAYER BET EQUATION

C_1-nC_5 Mixtures					
	Adsorption, v - Mg. Moles/Gm. Gel				
Mol Fraction n-Pentane	P_T = 1014 Psia	P_T = 699 Psia	P_T = 492 Psia	P_T = 354 Psia	P_T = 147 Psia
0.001	0.1958	0.246	0.2562	0.248	0.178
0.003	0.532	0.591	0.609	0.59	0.442
0.005	0.755	0.824	0.844	0.822	0.637
0.007	0.914	0.994	1.014	0.989	0.788

TABLE 13

n-HEXANE ADSORPTION CALCULATED
BY MONOLAYER BET EQUATION

C_1-nC_6 Mixtures					
	Adsorption, v - Mg. Moles/Gm. Gel				
Mol Fraction n-Hexane	P_T = 1014 Psia	P_T = 665 Psia	P_T = 445 Psia	P_T = 306 Psia	P_T = 120 Psia
0.001	0.433	0.516	0.54	0.524	0.3722
0.003	0.879	0.987	1.017	0.983	0.773
0.005	1.116	1.218	1.24	1.218	1.004
0.007	1.263	1.351	1.375	1.35	1.155
0.010	1.40	1.481	1.497	1.48	1.307

TABLE 14

DATA FOR LANGMUIR ISOTHERM PLOT
v_1/v_x vs P_1/P_x

Run	Peq., Psia	v_1/v_x*	P_1/P_x*
1	1014.0	21.0	531
2	1014.2	7.23	195.5
3	1014.1	6.6	156
4	1019.0	4.17	111.5
5	1014.0	2.77	73.9
6	1014.2	1.141	40.5
7	1014.3	1.552	50.6
8	1014.2	1.09	131.9
9	1014.3	3.21	296.4
10	1014.3	5.33	440
11	1014.3	1.407	155
12	1014.2	3.276	574
13	1014.3	2.964	438
13	1014.3	1.309	160.3
14	1014.1	2.404	252.5
15	1014.2	0.0	95.5

*Subscript 1 refers to methane,
Subscript x refers to other hydrocarbon.

TABLE 15

SLOPES, b, FROM FIGURE 36

nC_4 Adsorption

C_1-nC_4 Mixture

P_T, Psia	Slope, b	$(P_T)^{0.5}$
1014	0.00091	31.84
700	0.001982	26.44
500	0.00269	22.34
350	0.003475	18.7
265	0.00377	16.28
125	0.00488	11.18

TABLE 16

DATA FOR FIGURE 33 FROM
SMOOTHED CURVE IN FIGURE 32

y_4	x_4	K_4	$(K_4)^{0.5}$	X_T*	$1/X_T$
0.002	0.058	0.03446	0.184	0.00825	121.1
0.003	0.080	0.0375	0.1936	0.01187	84.3
0.004	0.10	0.0400	0.200	0.01522	65.6
0.006	0.142	0.04225	0.2056	0.02156	46.3
0.008	0.184	0.04350	0.2084	0.0279	35.8
0.010	0.226	0.04425	0.211	0.03412	29.3
0.012	0.267	0.04495	0.212	0.0404	24.74
0.014	0.308	0.04545	0.2132	0.0465	21.5
0.016	0.350	0.0457	0.2136	0.0529	18.9
0.018	0.391	0.04605	0.2144	0.0591	16.9
0.020	0.433	0.0462	0.2148	0.0654	15.3

*Values of X_T were calculated from values of v_4 from v_4 vs y_4 plot.

APPENDIX C

NOMENCLATURE

Capital Letters

A_i	Adsorbed area per mole of component i
B_r	Boiling point ratio
E_o	Defined by Equation (34)
E_j	Ratio of adsorbed surfaces s_{j+1}/s_j
$F_i(N_{il})$	Function of N_i to correct for deviations from ideal solution behavior in adsorbed phase
K,K',K''	Constants
K_{ADS}	Vapor-adsorbate equilibrium ratio, y/x
M	Molecular weight of gas
N	Number of molecules in system
N_i	BET adsorbed phase concentration of component i
$\bar{N}$	Avogadro's number
P, P_i	Partial pressure of component i
Peq.	Equilibrium pressure
P^o_i, P_o	Saturation vapor pressure of component i
P_r	Reduced pressure
P_x	Partial pressure of given component other than methane
P_T	Total system pressure
Q	Heat of adsorption
Q_1	Heat of adsorption of first layer
Q_v	Heat of vaporization of liquid adsorbate
R	Gas constant

S	Surface area of adsorbate
T	Absolute temperature
T_r	Reduced temperature
V	Volume
$\bar{V}$	Molal volume
V_i	Molal volume of saturated liquid at boiling point temperature corresponding to the adsorption pressure
X_T	Adsorption, grams/gram of gel
Z_T	Compressibility factor of mixture at T, P_T

Lower Case Letters

a	3-D van der Waals constant
a_2	2-D van der Waals constant
b	Energy constant in Langmuir isotherm
b_i	Langmuir energy constant for component i
b_2	2-D van der Waals constant
c_i, c	Pure component BET energy constants for component i
f, f_3, $\bar{f}^v$	fugacity
f^o	Pure component fugacity at P^o
f^o_L	Fugacity of pure component as saturated liquid at the adsorption temperature
f^o_V	Fugacity of pure component as vapor at the adsorption temperature and pressure
i, j	Running indices
k	Boltzmann's constant
k_1, k_2	Langmuir adsorption rate constants

k'_1, k'_2	Langmuir desorption rate constants
k'	Constant in Freundlich equation
n	Constant
n	BET number of adsorption layers
q_i	Heat of adsorption per mole of i on the bare surface of the solid
q_{ii}	Heat of adsorption per mole of i on a layer of pure i
v_o	Molar volume
v	Amount adsorbed
v_{mi}, v_m	Amount adsorbed when one monolayer is completed, for component i
v_x	Amount adsorbed for component other than methane
x	P/P^o
x_i	Mol fraction of component i in adsorbed phase
x'_i	Relative fugacity, f_i/f^o_i
y_i	Mol fraction of component i in gas phase
y_4, y_5, y_6	Mol fractions of n-Butane, n-Pentane, and n-Hexane, respectively

Greek Letters

α	Area in 2-D equations
α'	Relative volatility y_1x_2/y_2x_1
γ_{ij}	Surface fraction of layer j that is covered by component i
θ	Fraction of surface covered
θ^v	Function in Figures 7, 8, 9

μ	Number of molecules striking surface of adsorbent
π	2-D pressure
σ^o	Component area per mole
Σ	Specific surface area of solid
τ	Average length of time a molecule remains at the surface
τ_o	Time of oscillation of a molecule